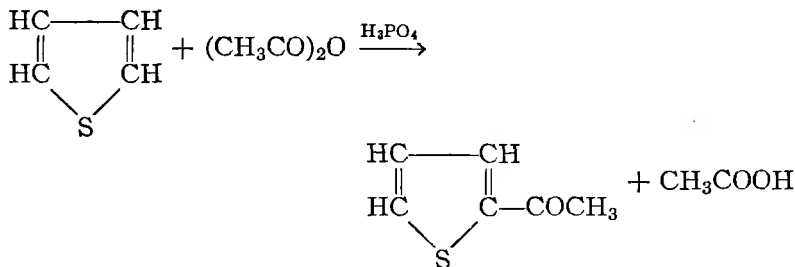


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2-ACETOTHIENONE

(Ketone, methyl 2-thienyl)



Submitted by ALVIN I. KOSAK and HOWARD D. HARTOUGH.

Checked by GEORGE T. GMITTER, F. LEE BENTON, and CHARLES C. PRICE.

1. Procedure

In a 1-l. three-necked flask fitted with a mechanical stirrer, a thermometer, and a reflux condenser are placed 168 g. (2 moles) (Note 1) of thiophene (Note 2) and 107 g. (1 mole) of 95% acetic anhydride (Note 3). The solution is heated to 70–75°, the source of heat is removed, and 10 g. (6 ml.) of 85% phosphoric acid is added with stirring. After 2–3 minutes an exothermic reaction occurs, and it is necessary to immerse the flask in a cold water bath to control the reaction. The boiling subsides in a few minutes; heat is again applied, and the mixture is refluxed for a total of 2 hours. The cooled mixture is washed successively with one 250-ml. portion of water and two 100-ml. portions of 5% sodium carbonate and is dried over anhydrous sodium sulfate. The orange-red liquid is distilled through a short fractionating column. After the removal of 76–80 g. of unchanged thiophene (b.p. 83–84°) by distillation at atmospheric pressure the residue is distilled under reduced pressure. The yield of 2-acetothienone, b.p. 89–90°/10 mm. (m.p. 9.2–10.5°; n_D^{20} 1.5662), is 93–100 g. (74–79%).

2. Notes

1. Acetic anhydride rather than thiophene may be used in excess, but the unchanged reagent cannot be recovered by the procedure given. With a 3:1 mole ratio of thiophene to anhydride the yield is of the order of 85%.

2. Commercial 99+% thiophene was employed.

3. The use of an equivalent amount of freshly distilled 100% acetic anhydride does not improve the yield.

3. Methods of Preparation

In addition to the methods of preparation given in connection with the procedure ¹ for the acetylation of thiophene with acetyl chloride in the presence of stannic chloride, 2-acetothienone has been prepared from thiophene and either acetyl chloride or acetic anhydride in the presence of iodine,² hydriodic acid,² silica-metal oxides,³ zinc chloride,⁴ or inorganic oxyacids.⁵ It has also been prepared from thiophene and acetic acid in the presence of hydrogen fluoride ⁵ or phosphorus pentoxide.⁶ The acylation in the presence of phosphorus pentoxide is particularly useful with higher aliphatic acids.⁶

¹ *Org. Syntheses* Coll. Vol. 2, 8 (1943).

² Hartough and Kosak, *J. Am. Chem. Soc.*, **68**, 2639 (1946).

³ Hartough, Kosak, and Sardella, *J. Am. Chem. Soc.*, **69**, 1014 (1947).

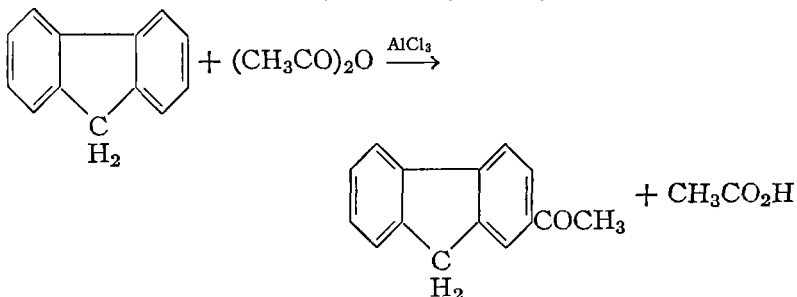
⁴ Hartough and Kosak, *J. Am. Chem. Soc.*, **69**, 1012 (1947).

⁵ Hartough and Kosak, *J. Am. Chem. Soc.*, **69**, 3093 (1947).

⁶ Hartough and Kosak, *J. Am. Chem. Soc.*, **69**, 3098 (1947).

2-ACETYLFLUORENE

(Ketone, 2-fluorenyl methyl)



Submitted by F. E. RAY and GEORGE RIEVESCHL, JR.

Checked by R. L. SHRINER and ARNE LANGSJOEN.

1. Procedure

Caution! Carbon disulfide, used as a solvent in this preparation, is highly inflammable; its vapor may ignite on contact with a hot laboratory steam line.

A 1-l. three-necked round-bottomed flask is fitted with a dropping funnel, a reflux condenser attached to a hydrogen chloride absorption trap,¹ and a very sturdy mechanical stirrer (Note 1), which may be of the mercury-sealed or rubber-sleeve type. In the flask are placed 350 ml. of dry carbon disulfide and 80 g. (0.48 mole) of fluorene (Note 2). The stirrer is started, and, after the fluorene has dissolved, 128 g. (0.96 mole) of anhydrous aluminum chloride is added in one portion. In the dropping funnel is placed 49.4 g. (0.48 mole) of redistilled acetic anhydride, and about 1 ml. of it is added dropwise to the vigorously stirred dark red reaction mixture. If the reaction does not start immediately it is initiated by warming the reaction flask in a water bath (Note 3). After the reaction has started, the balance of the acetic anhydride is added at such a rate that the carbon disulfide refluxes gently; about 45–55 minutes is required. When approximately one-half of the acetic anhydride has been added an addition complex sepa-

rates as a heavy mass which makes stirring very difficult. However, stirring must be maintained to prevent excessive local reaction at the point of introduction of the acetic anhydride. The mixture is stirred and refluxed on the water bath for an hour after the addition of the acetic anhydride is complete.

The dark green mass is collected on a large Büchner funnel and transferred as quickly as possible (Note 4) to a 1-l. beaker in which it is stirred mechanically for 10 minutes with 300 ml. of carbon disulfide (Note 5). The solid is again collected and washed on the filter with two 50-ml. portions of carbon disulfide (Note 6) and with one 100-ml. portion of petroleum ether (b.p. 28–35°). The resulting granular aluminum chloride complex is decomposed by portionwise addition to a well-stirred mixture of 800 ml. of water and 30 ml. of concentrated hydrochloric acid in a 2-l. beaker under a hood. Each portion is allowed to hydrolyze before the next is added. The hydrolysis mixture should not be cooled. The crude 2-acetylfluorene is collected on a filter and washed three times with 100-ml. portions of water. After drying in an oven at 100° for 3 hours the light orange ketone weighs 83–95 g. (83–95%) and melts over the range 113–117° (Note 7). This crude product is transferred to a 2-l. round-bottomed flask containing 800 ml. of 95% ethanol and 5 g. of decolorizing carbon. The mixture is refluxed for 1 hour and filtered hot. On cooling the filtrate deposits 71–83 g. of light tan solid melting at 120–123°. A second recrystallization from 800 ml. of ethanol yields 55–63 g. (55–63%) of a light cream-colored powder which melts at 124–126° and which is pure enough for most purposes (Note 8).

2. Notes

1. The stirrer, which may be of either the half-round or the propeller type, must be of heavy construction and must be driven by one of the more powerful laboratory stirring motors. Agitation must be maintained throughout the reaction period.

2. If technical fluorene (m.p. 103–107°) from Eastman Kodak Company or the Barrett Company is used, much difficulty is experienced in the purification of the product. Technical fluorene can be rendered suitable for the preparation by recrystallization

from hot 95% ethanol (1 l. for 150 g.). The once-recrystallized material melts at 114–115° (lit. 116°).

3. It is necessary to make sure that the reaction has started before the addition of more acetic anhydride in order to prevent a violent reaction.

4. Exposure to the air causes the addition product to become sticky and difficult to handle.

5. Unless this operation can be conducted at a point remote from flames, hot plates, and other sources of heat, a flask should be substituted for the open beaker.

6. The carbon disulfide extracts unchanged fluorene and other impurities. Any lumps in the crude material should be crushed during the first washing. The rinsing with petroleum ether removes the last of the carbon disulfide.

7. This crude 2-acetylfluorene is completely soluble in carbon disulfide and thus is free of the insoluble 2,7-diacetylfluorene. It may be used directly for the oxidation to fluorenone-2-carboxylic acid (p. 63).

8. The pure product ² melting at 128–129° (cor.) can be obtained in 42–45% yield by two more recrystallizations from 400-ml. portions of acetone. Pure 2-acetylfluorene has also been reported ³ as melting at 132°, but this value has not been checked.

3. Methods of Preparation

2-Acetylfluorene has been prepared by the reaction of fluorene with acetic anhydride ^{2,4} or with acetyl chloride ^{3,5} in the presence of aluminum chloride in carbon disulfide or in nitrobenzene. When nitrobenzene is employed as the solvent it must be removed by a time-consuming steam distillation, and the use of acetyl chloride as a reagent leads to the formation of considerable amounts of 2,7-diacetylfluorene.

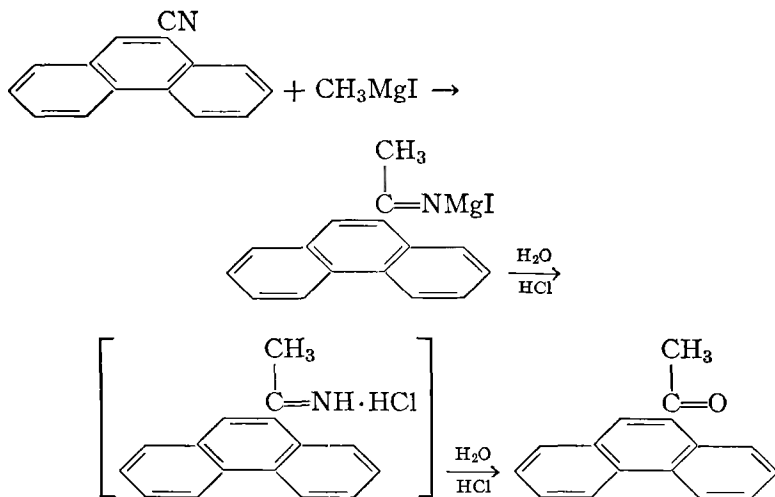
¹ *Org. Syntheses* Coll. Vol. 2, 4¹ (1943).

² Bachmann and Sheehan, *J. Am. Chem. Soc.*, **62**, 2688 (1940).

³ Dziewonski and Schnayder, *Bull. intern. acad. polon. sci.*, **1930A**, 529 [*C.A.*, **25**, 5416 (1931)].

⁴ Ray and Rieveschl, *J. Am. Chem. Soc.*, **65**, 836 (1943).

⁵ Ardashev, Lomovatskaya, and Kacher, *J. Applied Chem. U.S.S.R.*, **11**, 1344 (1938) [*C.A.*, **33**, 5844 (1939)].

9-ACETYLPHENANTHRENE**(Ketone, methyl 9-phenanthryl)**

Submitted by JOSEPH E. CALLEN, CLINTON A. DORN-FELD, and GEORGE H. COLEMAN.¹

Checked by ROBERT E. CARNAHAN and HOMER ADKINS.

1. Procedure

A dry 12-l. three-necked flask is equipped with an efficient motor-driven stirrer (Note 1), a nitrogen inlet tube, a large Allihn condenser, and a 1-l. separatory funnel. Both the condenser and the funnel are provided with calcium chloride drying tubes. To the flask is added 146 g. (6 gram atoms) of magnesium turnings (Note 2), and nitrogen gas, first bubbled through concentrated sulfuric acid, is passed in to displace the air. During the reaction the nitrogen atmosphere is maintained. The magnesium is covered with 200 ml. of anhydrous ether, and a few milliliters of a solution of 852 g. (6 moles) of methyl iodide in 1 l. of anhydrous ether is added from the separatory funnel. The reaction starts spontaneously, and then the remainder of the methyl iodide solu-

tion is added slowly. When the reaction is complete (Note 3), 4 l. of dry benzene is added, a condenser is arranged for downward distillation, and about 1.2 l. of solvent is distilled (Note 4). The condenser is changed to a reflux position, 609 g. (3 moles) of 9-cyanophenanthrene (p. 34) is added quickly through a powder funnel, and the mixture is heated and stirred under reflux for 3 hours. It is then cooled in an ice bath to 0°, 3 l. of cold 6 *N* hydrochloric acid is slowly added (*Caution!*) from a separatory funnel with stirring, and the mixture is refluxed for 6 to 8 hours (Note 5).

After cooling, the layers are separated, the organic layer is washed with dilute sodium bicarbonate solution and placed in a flask equipped for distillation, and the solvent is distilled. The oily residue is transferred while still warm to a 1-l. Claisen flask, and the product is distilled under reduced pressure; b.p. 190–200°/2.5 mm. (168–170°/1 mm.). The yield is 400–430 g. (61–65%). The distilled ketone is recrystallized once from ethanol (1.5–2 l.) to yield 345–390 g. (52–59%) of 9-acetylphenanthrene of m.p. 73–74°.

2. Notes

1. If a 12-l. three-necked flask is not available, a three-way adapter tube may be used in making the necessary connections. Although a mercury seal may be used, a glycerol-rubber tube seal ² is adequate.
2. The checkers operated on one-tenth the scale specified.
3. In several runs the Grignard reagent was filtered at this point, but the improvement in yield was not appreciable.
4. The addition of benzene and distillation of part of the solvent raises the reaction temperature.
5. The oily layer of ketimine hydrochloride usually dissolves during 6 hours' refluxing.

3. Methods of Preparation

The method described above is a modification of that of Bachmann and Boatner.³ 9-Acetylphenanthrene has also been

obtained by a Claisen condensation of methyl phenanthrene-9-carboxylate with ethyl acetate followed by scission of the resulting phenanthroylacetic ester,⁴ by the reaction of 9-phenanthrylmagnesium bromide with acetyl chloride,⁵ and by dehydrogenation of 9-acetyl-1,2,3,4-tetrahydrophenanthrene by heating with sulfur.⁶

¹ Work done under contract with the Office of Scientific Research and Development.

² *Org. Syntheses*, **21**, 40 (1941).

³ Bachmann and Boatner, *J. Am. Chem. Soc.*, **58**, 2098 (1936).

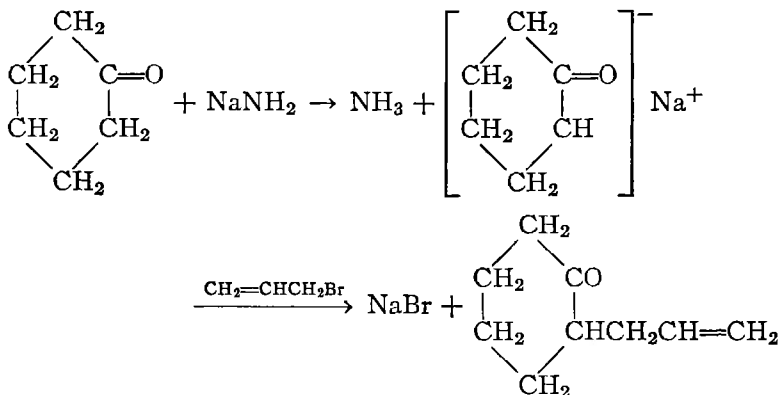
⁴ Mosettig and van de Kamp, *J. Am. Chem. Soc.*, **55**, 3445 (1933).

⁵ Miller and Bachman, *J. Am. Chem. Soc.*, **57**, 768 (1935).

⁶ Bachmann and Struve, *J. Org. Chem.*, **4**, 476 (1939).

2-ALLYLCYCLOHEXANONE

(Cyclohexanone, 2-allyl-)



Submitted by CALVIN A. VANDERWERF and LEO V. LEMMERMAN.

Checked by ARTHUR C. COPE and THEODORE T. FOSTER.

1. Procedure

Approximately 1.5 l. of anhydrous liquid ammonia is introduced into a dry 5-l. three-necked flask fitted with a sealed mechanical stirrer and an efficient reflux condenser which is con-

nected through a soda-lime tube to a gas-absorption trap.¹ Freshly cut sodium (47.2 g., 2.05 gram atoms) is converted to sodium amide by addition to the liquid ammonia in the presence of a small amount of ferric nitrate, according to a procedure previously described in detail.² A 1-l. dropping funnel and a gas inlet tube connected to a source of dry nitrogen are attached to the third neck of the flask, and, after the blue color of the solution has disappeared and a gray suspension of sodium amide remains (Note 1), 1.2 l. of dry ether is added as rapidly as the rate of vaporization of ammonia will permit. The ammonia is removed by warming the flask on a steam bath until refluxing of the ether occurs. Cyclohexanone (Note 2) (220 g., 2.24 moles) is added through the dropping funnel (Note 3), and the mixture is stirred and heated under reflux on a steam bath for 3 hours. Nitrogen is then introduced through the gas inlet tube to maintain an inert atmosphere (Note 4), and the mixture is cooled in an ice bath. A solution of 246 g. (2.03 moles) of allyl bromide (Note 5) in 1 l. of anhydrous ether is added rapidly through the dropping funnel with stirring. If the reaction does not start soon after the completion of this addition the mixture is warmed cautiously on the steam bath. When the exothermic reaction has started it is controlled by cooling in the ice bath while refluxing continues for 20–30 minutes. The mixture is finally heated under reflux on the steam bath for 3 hours.

The mixture is cooled in an ice bath, any sodium or sodium amide which may remain in the necks of the flask is scraped into the reaction mixture with a spatula, and enough water is added to dissolve the sodium bromide. The ether layer is separated and combined with five 100-ml. ether extracts of the aqueous phase, washed with 150 ml. of saturated sodium chloride solution, and dried over anhydrous sodium sulfate. The ether is removed by distillation, and the residue is fractionated carefully under reduced pressure through a 4-ft. heated column packed with glass helices and fitted with a total-condensation variable take-off head. The yield of 2-allylcyclohexanone boiling at 90–92°/17 mm. is 153–174 g. (54–62%). In addition, 28–38 g. of unchanged cyclohexanone boiling at 51–52°/17 mm., 15–35 g. of diallylcyclohexa-

none boiling at 113–124/17 mm., and small intermediate fractions are obtained.

2. Notes

1. The conversion of the sodium to sodium amide requires 30–90 minutes. More liquid ammonia may be added if too much is lost by vaporization before the conversion is complete.

2. Redistilled cyclohexanone, b.p. 154–156°, was used.

3. The submitters obtained equally good results by adding 80 g. (2.05 moles) of freshly prepared finely powdered sodium amide³ in portions to a solution of the cyclohexanone in 1.2 l. of dry ether, heating under reflux for 3 hours, and continuing the preparation in the manner described.

4. The submitters state that the yield is increased appreciably if a nitrogen atmosphere is maintained after this point. Loss of ether may be avoided by stopping the flow of nitrogen when refluxing begins.

5. Allyl bromide was dried over calcium chloride and redistilled, b.p. 70–71.5°.

3. Methods of Preparation

2-Allylcyclohexanone has been prepared by the direct alkylation of the sodium derivative of cyclohexanone with allyl iodide, sodium amide having been used in the preparation of the sodium enolate,⁴ and by ketonic hydrolysis of ethyl 1-allyl-2-ketocyclohexanecarboxylate, prepared by alkylation of ethyl 2-ketocyclohexanecarboxylate.^{5, 6}

¹ *Org. Syntheses* Coll. Vol. 2, 4 (1943).

² *Org. Syntheses*, 25, 25 (1945).

³ *Org. Syntheses*, 20, 86 (1940).

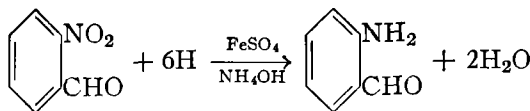
⁴ Cornubert, *Ann. chim.*, [9] 16, 145 (1921).

⁵ Cope, Hoyle, and Heyl, *J. Am. Chem. Soc.*, 63, 1848 (1941).

⁶ Grewe, *Ber.*, 76, 1075 (1943).

o-AMINOBENZALDEHYDE

(Anthranilaldehyde)

Submitted by LEE IRVIN SMITH and J. W. OPIE.¹

Checked by CLIFF S. HAMILTON, C. W. WINTER, and HARRY M. WALKER.

1. Procedure

A 1-l. three-necked flask is employed as a reaction vessel from which the product can be steam-distilled *immediately* after completion of the reaction (Note 1). It is convenient to arrange the apparatus for the reaction and that for the steam distillation on the same steam bath, with provision for the rapid connection of the flask to the distillation assembly at the desired time. For use as a reaction vessel the flask is mounted on a steam bath and fitted with a mechanical stirrer and a reflux condenser; the third neck is closed by a cork.

In the steam-distillation assembly (Note 1) one of the small necks of the flask is fitted with a steam-inlet tube, connected through a water trap to a steam line; the other small neck is closed by a cork. The central neck is fitted to a Kjeldahl trap leading to a 50-cm. Allihn condenser set downward and connected in series to a 50-cm. Liebig condenser. The second condenser leads to a 500-ml. three-necked flask used as the receiver. The receiving flask is immersed in an ice bath and fitted with an Allihn reflux condenser.

When all the apparatus has been set up and tested the flask is connected to the reaction assembly, and 175 ml. of water, 105 g. (0.38 mole) of ferrous sulfate heptahydrate, 0.5 ml. of concentrated hydrochloric acid, and 6 g. (0.04 mole) of *o*-nitrobenzaldehyde² are introduced in the order given. The stirrer is then started, and the flask is heated by means of the steam bath. When the temperature of the mixture reaches 90°, 25 ml. of con-

centrated ammonium hydroxide is added in one portion, and at 2-minute intervals three 10-ml. portions of ammonium hydroxide are added. Stirring and heating are continued throughout. The total reaction time is 8–10 minutes.

Immediately after the addition of the last portion of ammonium hydroxide, the reflux condenser and stirrer are removed and the flask is connected to the steam-distillation assembly. The mixture is steam-distilled as rapidly as possible, and two 250-ml. fractions of distillate are collected during a period of 10–13 minutes (Note 2). The first fraction is saturated with sodium chloride, and the solution is stirred at 5° until precipitation appears complete. The solid is collected on a Büchner funnel and dried in the air. The product weighs 2.72–3.11 g. (57–65%) and melts at 38–39°. The second fraction of the distillate is saturated with sodium chloride and combined with the filtrate remaining from the first fraction. The combined solution is extracted with two 45-ml. portions of ether. The combined ether extract is filtered, dried over anhydrous sodium sulfate, and concentrated by distillation, finally under reduced pressure. The residue solidifies on cooling and weighs 0.6–1.0 g.; it can be purified by steam distillation from 40–50 ml. of saturated sodium chloride solution until 100 ml. of distillate is collected, saturation of the distillate with sodium chloride, cooling, and filtration. The pure product so obtained weighs 0.42–0.87 g. The total yield (Note 3) is 3.3–3.6 g. (69–75%).

2. Notes

1. Rapid removal of the product from the reaction mixture is essential to the success of this preparation. The steam-distillation assembly should be sturdily constructed, with all parts except the distilling flask in place at the time the reaction is started. To ensure the proper fitting of the distilling flask it is convenient to construct the distillation apparatus with the flask in place and, after testing of the apparatus, to remove the flask and incorporate it into the reaction assembly.

2. The first fraction is drawn into a round-bottomed flask through a tube inserted into the third neck of the receiver (by the

use of a water pump or a suction line) without interruption of the distillation.

3. The submitters have obtained yields of about 70% in runs eight times as large as that described. This amino aldehyde undergoes self-condensation on standing, especially in a desiccator, and so the product should be used immediately.

3. Methods of Preparation

o-Aminobenzaldehyde has been obtained from its oxime by the action of ferric chloride;³ the oxime was obtained by reduction of *o*-nitrobenzaldoxime.⁴ *o*-Aminobenzaldehyde has also been obtained from *o*-aminobenzyl alcohol by the action of sodium sulfide⁵ or by the action of zinc dust and alkali;⁶ and from *o*-nitrobenzylaniline or N-(2-nitrobenzyl)-sulfanilic acid by the action of alkali sulfides and sulfur.⁷ The aldehyde results in small amounts from the action of alkali alone upon *o*-nitrobenzyl alcohol⁸ and from the action of ferrous sulfate and ammonia upon anthranil.⁹ The only preparative methods involve the reduction of *o*-nitrobenzaldehyde with ferrous sulfate and ammonia.^{9,10} Catalytic reduction of *o*-nitrobenzaldehyde has been reported to yield *o*-aminobenzaldehyde,¹¹ but the method was not successful in the hands of the submitters.

¹ Work done under contract with the Office of Scientific Research and Development.

² *Org. Syntheses*, **24**, 75 (1944).

³ Gabriel, *Ber.*, **15**, 2004 (1882).

⁴ Gabriel and Meyer, *Ber.*, **14**, 2339 (1881); *Ber.*, **36**, 803 (1903).

⁵ Ger. pat. 106,509 (*Chem. Zentr.*, **1900**, I, 1084).

⁶ Freundler, *Compt. rend.*, **136**, 371 (1903); **138**, 1425 (1904); *Bull. soc. chim. France*, [3] **31**, 876 (1904).

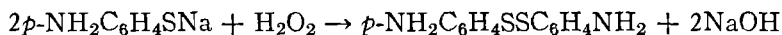
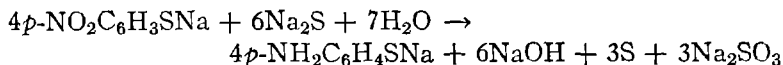
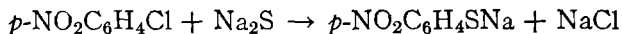
⁷ Ger. pat. 99,542, 100,968 (*Chem. Zentr.*, **1899**, I, 238, 958); Cohn and Springer, *Monatsh.*, **24**, 95 (1903); Friedländer and Lenk, *Ber.*, **45**, 2084 (1912).

⁸ Freundler, *Bull. soc. chim. France*, [3] **31**, 879 (1904); Carré, *Compt. rend.*, **140**, 664 (1905); *Bull. soc. chim. France*, [3] **33**, 1162, 1165 (1905); *Ann. chim.*, [8] **6**, 409, 413 (1905).

⁹ Friedländer, *Ber.*, **15**, 2573 (1882).

¹⁰ Friedländer and Göhring, *Ber.*, **17**, 456 (1884); Bamberger, *Ber.*, **60**, 319 (1927).

¹¹ Ruggli and Schmidt, *Helv. Chim. Acta*, **18**, 1235 (1935); Nord, *Ber.*, **52**, 1711 (1919).

***p*-AMINOPHENYL DISULFIDE**(Aniline, *p,p'*-dithiodi-)

Submitted by CHARLES C. PRICE and GARDNER W. STACY.

Checked by CLIFF S. HAMILTON and THEO BROWN.

1. Procedure

In a 5-l. round-bottomed flask equipped with a reflux condenser and a mechanical stirrer are placed 236 g. (1.5 moles) of *p*-chloronitrobenzene, 960 g. (4 moles) of sodium sulfide nonahydrate, and 2.5 l. of water. With rapid agitation, the reaction mixture is slowly heated to the reflux temperature (Note 1). Heating is continued over a period of 20 hours.

The mixture is cooled to about 15° and filtered on a large Büchner funnel to remove insoluble material, chiefly *p*-chloroaniline. The filtrate is placed in a 5-l. three-necked flask, equipped with a dropping funnel, a mechanical stirrer, and a downward condenser; it is concentrated by distillation over a flame to a volume of 1.5 l. (Note 2). The condenser is replaced by a thermometer, the stirrer is started, and the dropping funnel is charged with 230 ml. of 30% hydrogen peroxide. The temperature of the reaction mixture is maintained at 65–70° while the hydrogen peroxide is added dropwise over a period of about 2 hours (Note 3).

The reaction mixture is cooled, and the crude *p*-aminophenyl disulfide, obtained as spherical lumps amounting to 125–150 g. and melting at 73°, is collected on a Büchner funnel. It is dissolved in 1 l. of hot ethanol, and the small amount of insoluble material is removed by filtration. To the hot solution is then

added 800 ml. of water containing several grams of sodium hydro-sulfite to prevent discoloration of the solution by oxidation. The solution is cooled, and an additional 700 ml. of water is added with stirring to reduce the solubility of the product. The crystal-line precipitate is removed by filtration and dried in a vacuum desiccator. The yield of pure product melting at 75–76° is 108–120 g. (58–64%).

2. Notes

1. The reaction mixture should not be heated too strongly as the temperature nears the boiling point, since the initial reaction is quite vigorous.

2. Some *p*-chloroaniline is removed by steam distillation during the concentration.

3. At first the solution becomes cloudy, and later large yellow globules begin to accumulate. Frequent cooling is required to maintain the temperature within the specified range.

3. Methods of Preparation

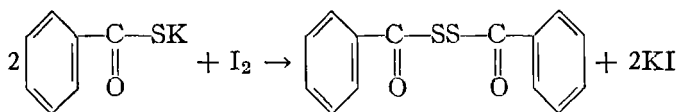
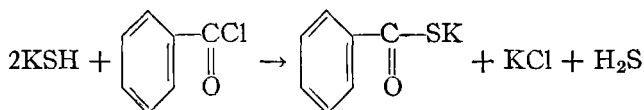
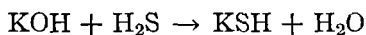
The procedure outlined is essentially that of Lantz¹ except for the use of hydrogen peroxide rather than air in the final oxidation. *p*-Aminophenyl disulfide has also been prepared by heating a mixture of aniline, aniline hydrochloride, and sulfur,² and by the reduction of *p*-nitrophenyl disulfide with stannous chloride.³

¹ Lantz, Fr. pat. 714,682 (*Chem. Zentr.*, **1932**, I, 1828).

² Hinsberg, *Ber.*, **38**, 1131 (1905).

³ Shukla, *J. Indian Inst. Sci.*, **10**, 33 (1927).

BENZOYL DISULFIDE



Submitted by ROBERT L. FRANK and JAMES R. BLEGEN.¹

Checked by ARTHUR C. COPE and FRANK S. FAWCETT.

1. Procedure

A solution of 315 g. (5.62 moles) of potassium hydroxide in 3150 ml. of commercial absolute ethanol is prepared with mechanical stirring in a 5-l. three-necked round-bottomed flask. The flask is fitted with a 500-ml. dropping funnel and a gas inlet tube extending to the bottom of the flask, and hydrogen sulfide is passed in through the inlet tube with stirring until the solution is saturated and no longer gives an alkaline reaction with phenolphthalein (Notes 1, 2). The mixture is cooled to 10–15° by means of an ice bath, and 346.5 g. (2.46 moles) of redistilled benzoyl chloride is introduced dropwise with stirring while the temperature is kept below 15°. The potassium chloride which precipitates during the addition (Note 3) is separated by filtration with suction through a Büchner funnel and is washed with about 200 ml. of ethanol (Note 4). The filtrate and washings are cooled to 10–15°, and solid iodine is added slowly, with constant agitation, until a slight excess is present, as shown by a faint permanent coloration of the solution. The amount of iodine required varies from 336 g. to 407 g. (1.32–1.61 moles) (Note 5). Benzoyl disulfide precipitates during the addition. It is collected on a

filter and washed with 750 ml. of 95% ethanol followed by 3 l. of water. The crude product, after drying at room temperature, or in an oven at a temperature which does not exceed 60° (Note 6), weighs 325–333 g.

The crude material is dissolved with stirring in 910 ml. of ethylene chloride heated to 60° in a water bath (Note 6). The solution is allowed to cool to room temperature, 122 ml. of a saturated aqueous solution of sodium bicarbonate is added to the resulting slurry, and the mixture is stirred for 1 hour (Note 7). The layers are then separated in a separatory funnel, and the ethylene chloride slurry is heated to 60° in a water bath. The resulting solution is filtered through a small cotton plug in a preheated funnel. Absolute ethanol (313 ml.) is added to the filtrate, and the mixture is stored in an ice box overnight while the product crystallizes. The crystals are collected on a filter and washed with 40 ml. of ether. The product is recrystallized by dissolving it in ethylene chloride (3.0 ml. per g. of product) heated to 60° in a water bath (Note 6) and cooling. The yield of white to light pink plates, m.p. 129–130°, is 230–246 g. (68–73%).

2. Notes

1. It is convenient during this step to use the dropping funnel as an exhaust tube by attaching its upper end to a gas-absorption trap. If this is not done, the preparation should be conducted in a well-ventilated hood.

2. The gas inlet tube should be of moderately large diameter or it may become plugged with crystals during the latter stages of the saturation with hydrogen sulfide.

3. Stirring is discontinued after the benzoyl chloride has been added. The precipitate of potassium chloride can be separated more easily if the mixture is allowed to stand overnight before filtration.

4. After the filtration and washing, the application of suction is continued until bubbles of hydrogen sulfide no longer form in the filtrate. Much of the excess hydrogen sulfide is removed during the filtration.

5. The amount of iodine required is presumed to vary according to the presence of variable amounts of hydrogen sulfide and to the extent of oxidation by atmospheric oxygen. In one unsatisfactory preparation in which a relatively large amount of hydrogen sulfide must have remained in the solution a total of 493 g. (1.94 moles) of iodine was required and the final product contained free sulfur.

6. If the temperature exceeds 60°, discoloration occurs and the product cannot be decolorized by recrystallization or treatment with activated charcoal.

7. This operation is carried out at room temperature because heating in the presence of alkalies decomposes benzoyl disulfide.

3. Methods of Preparation

Benzoyl disulfide has been obtained by the reaction of benzoyl chloride with hydrogen sulfide,² hydrogen disulfide,³ hydrogen trisulfide,^{3,4} potassium sulfide,⁵ sodium disulfide,⁶ lead sulfide,⁷ sodium hydrosulfite,⁸ sodium thiosulfate,⁹ sulphydrylmagnesium bromide,¹⁰ and thiobenzamide.¹¹ It is also formed by reaction of benzoic anhydride with hydrogen sulfide.¹² The better preparative methods involve the oxidation of thiobenzoic acid by means of air,^{7,13,14} hydrogen peroxide^{15,16} or sulfur monochloride,¹⁷ or of the sodium or potassium salt by means of air,^{16,18} chlorine,¹⁹ iodine,^{7a,14,15,20,21} copper sulfate,^{7,16} potassium ferricyanide,^{7,16,22} or ferric chloride.^{7,16}

¹ Work done under contract with the Office of Rubber Reserve.

² Szperl, *Roczniki Chem.*, **10**, 510 (1930) [*C.A.*, **25**, 503 (1931)].

³ Bloch and Bergmann, *Ber.*, **53**, 961 (1920).

⁴ Bergmann, Dreyer, and Radt, *Ber.*, **54**, 2139 (1921).

⁵ Bergmann, *Ber.*, **53**, 979 (1920).

⁶ Braker, U. S. pat. 2,154,488 [*C.A.*, **33**, 5415 (1939)].

⁷ (a) Engelhardt, Latschinoff, and Malyscheff, *Z. Chem.*, **4**, 353 (1868); (b) Engelhardt and Latschinoff, *Z. Chem.*, **4**, 455 (1868).

⁸ Binz and Marx, *Ber.*, **40**, 3855 (1907).

⁹ Westlake and Dougherty, *J. Am. Chem. Soc.*, **67**, 1861 (1945).

¹⁰ Mingoia, *Gazz. chim. ital.*, **55**, 718 (1925).

¹¹ Musajo and Amoruso, *Gazz. chim. ital.*, **67**, 301 (1937).

¹² Mosling, *Ann.*, **118**, 303 (1861).

¹³ Cloëz, *Ann.*, **115**, 23 (1860).

¹⁴ Weigert, *Ber.*, **36**, 1007 (1903).

¹⁵ Moness, Lott, and Christiansen, *J. Am. Pharm. Assoc., Sci. Ed.*, **25**, 397 (1936).

¹⁶ Shelton and Rider, *J. Am. Chem. Soc.*, **58**, 1282 (1936).

¹⁷ Chakravarti, *J. Chem. Soc.*, **1923**, 964.

¹⁸ Rider and Shelton, U. S. pat. 2,028,246 [*C.A.*, **30**, 1811 (1936)].

¹⁹ Bergmann and Bloch, *Ber.*, **53**, 977 (1920).

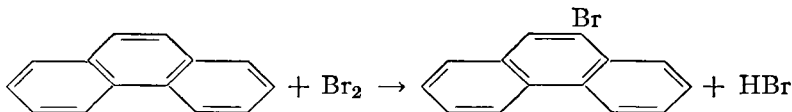
²⁰ Amberg and Brunsting, *Military Surgeon*, **88**, 617 (1941) [*C.A.*, **35**, 5643 (1941)].

²¹ Bloch, *Compt. rend.*, **204**, 1342 (1937).

²² Fromm and Palma, *Ber.*, **39**, 3317 (1906); Fromm and Schmoldt, *Ber.*, **40**, 2861 (1907).

9-BROMOPHENANTHRENE

(Phenanthrene, 9-bromo-)



Submitted by CLINTON A. DORNFELD, JOSEPH E. CALLEN, and GEORGE H. COLEMAN.¹

Checked by ROBERT E. CARNAHAN and HOMER ADKINS.

1. Procedure

A. Purification of technical phenanthrene. One and one-half kilograms of technical 90% phenanthrene is dissolved in 9 l. of ethanol in a 12-l. flask on a steam bath, and the hot solution is decanted from any insoluble material. The product crystallizes upon cooling of the solution. One kilogram of the crystallized product is dissolved in 2.2 l. of hot glacial acetic acid in a 5-l. three-necked flask provided with an efficient reflux condenser and a dropping funnel. To the boiling solution is gradually added 72 ml. of an aqueous solution containing 60 g. of chromic anhydride, and then 30 ml. of concentrated sulfuric acid is added slowly from the dropping funnel. The solution is refluxed for 15 minutes. The hot solution is then poured with vigorous stirring into 4.5 l. of water in a 12-l. round-bottomed flask. After cooling, the mixture is filtered, and the product is washed with water and air-

dried. The product is distilled (Note 1) at 148–149°/1 mm. The distillate is recrystallized from ethanol to give 800–900 g. of nearly white phenanthrene, m.p. 98.7–99°.

B. *9-Bromophenanthrene*. One kilogram (5.6 moles) of pure phenanthrene (Note 2) is dissolved in 1 l. of dry carbon tetrachloride in a 5-l. three-necked flask. A 500-ml. dropping funnel, a reflux condenser (with tube to conduct evolved hydrogen bromide to the hood), and an efficient motor-driven sealed stirrer (Note 3) are attached. The mixture is heated at gentle reflux with stirring, and 900 g. (5.64 moles) of bromine is added from the dropping funnel over a period of about 3 hours. After stirring at gentle reflux for 2 additional hours, during which most of the remaining hydrogen bromide is evolved, the reaction mixture is placed in a Claisen flask and the solvent is distilled at a pressure of 10–30 mm. The flask containing the residue is then provided with a fine capillary inlet tube, a thermometer, and a 2-l. distilling flask as receiver. The impure 9-bromophenanthrene is distilled (Note 4), and the material boiling at 177–190°/2 mm. is collected. The yield is 1300–1360 g. (90–94%), m.p. 54–56° (Notes 5 and 6).

2. Notes

1. Since the melting point of phenanthrene is relatively close to its boiling point under the pressure of the distillation, it is necessary to employ an apparatus so constructed that the solidified distillate will not clog the outlet tube. The submitters used a 2-l. modified Claisen flask attached directly, with a 14-mm. glass tube, to a 2-l. round-bottomed flask. The checkers used a similar all-glass apparatus.

2. The checkers used from 100 to 250 g. of phenanthrene with corresponding reductions of other quantities specified in the procedure.

3. A glycerol-rubber tube seal of the type described,² but made with Neoprene rather than natural rubber, is very satisfactory.

4. The flask may be supported on a wire gauze and heated directly with a Fisher or Meker burner. A modified Claisen flask equipped with a short column is desirable, but an ordinary

Claisen flask can be used if the heating is carefully controlled to prevent impure bromophenanthrene from splashing over. The oil pump should be protected with the usual Dry Ice trap and with a potassium hydroxide tower to absorb hydrogen bromide. Even in runs in which the carbon tetrachloride solution was washed successively with sodium bisulfite, sodium carbonate, and water, much hydrogen bromide was evolved during distillation.

5. If the distillation is performed carefully the product is probably sufficiently pure for most purposes without recrystallization. 9-Bromophenanthrene may be recrystallized from ethanol (about 10 ml. per g.).

6. In runs of one-tenth the scale specified, the product obtained by the checkers had a melting point of 50–55° when yields above 90% were obtained. The yields were about 10% lower when 9-bromophenanthrene of melting point 54–56° was produced. The yield of recrystallized compound, melting at 65–66°, as obtained by the checkers, was 60% of the theoretical.

3. Methods of Preparation

The procedure for the purification of technical phenanthrene is that of W. E. Bachmann ³ with slight modification.

The procedure described for the preparation of 9-bromophenanthrene is an adaptation of that described by Henstock,⁴ who effected the bromination at various temperatures and in different solvents but gave little experimental detail. Other methods ⁵ of preparation involve the formation and isolation of phenanthrene dibromide and its subsequent conversion to 9-bromophenanthrene by heating.

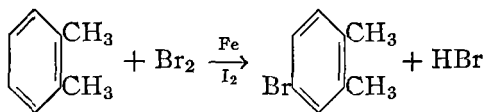
¹ Work done under contract with the Office of Scientific Research and Development.

² *Org. Syntheses*, **21**, 40 (1941).

³ Bachmann, *J. Am. Chem. Soc.*, **57**, 557 (1935).

⁴ Henstock, *J. Chem. Soc.*, **123**, 3097 (1923).

⁵ Bachmann, *J. Am. Chem. Soc.*, **56**, 1365 (1934); Hayduck, *Ann.*, **167**, 181 (1873); Anschutz, *Ber.*, **11**, 1217 (1878); Austin, *J. Chem. Soc.*, **93**, 1763 (1908); Sundqvist, *Ann.*, **308**, 126 (1913); Miller and Bachman, *J. Am. Chem. Soc.*, **57**, 768 (1935); Mosettig and May, *J. Org. Chem.*, **11**, 15 (1946); Goldberg, Ordas, and Carsh, *J. Am. Chem. Soc.*, **69**, 260 (1947).

4-BROMO-*o*-XYLENE**(*o*-Xylene, 4-bromo-)**

Submitted by W. A. WISANSKY and S. ANSBACHER.

Checked by N. L. DRAKE, WILKINS REEVE, and JOHN STERLING, JR.

1. Procedure

In a 1-l. three-necked flask having ground-glass joints are placed 500 g. (569 ml., 4.72 moles) of *o*-xylene, 12 g. of clean iron filings, and a crystal of iodine (Note 1). The flask is fitted with a dropping funnel, a stirrer (Note 2), and a condenser; a thermometer is suspended through the condenser on a platinum or Nichrome wire and arranged so that the bulb extends beneath the surface of the liquid. The top of the condenser is connected to a gas-absorption trap.¹ The mixture is stirred and cooled in an ice-salt mixture, preferably under a hood. Six hundred and sixty grams (4.13 moles) of bromine is added dropwise over a 3-hour period; during this time the internal temperature is maintained at 0° to -5° (Note 3). After all the bromine has been added the reaction mixture is allowed to stand overnight. It is poured into water and washed successively with a 500-ml. portion of water, two 500-ml. portions of 3% sodium hydroxide solution (Note 4), and one 500-ml. portion of water. The product is then steam-distilled; about 8 l. of distillate is collected (Note 5). The organic layer is separated from the water and dried over calcium chloride. The 4-bromo-*o*-xylene is distilled through a short column under reduced pressure, and the fraction boiling at 92-94°/14-15 mm. (n_D^{22} 1.5558) is collected. The yield is 720-745 g. (94-97%, based on bromine) (Note 6).

2. Notes

1. Essentially the same yield results if only one of the catalysts (iron or iodine) is used.

2. The checkers used a glycerol-sealed stirrer.

3. In experiments in which the temperature of the reaction mixture was allowed to rise as high as $+10^{\circ}$, the submitters noted a slight increase in the amount of dibromo-*o*-xylene formed.

4. A dilute sodium bisulfite solution may be used instead of the alkali in this washing.

5. Near the end of the steam distillation a white waxy product begins to collect in the condenser. This is apparently a dibromo-*o*-xylene.

6. This material is of sufficient purity for most uses, including the conversion to 3,4-dimethylaniline (p. 46). It is reported ² that the boiling point of the product can be raised slightly (from $211\text{--}212^{\circ}$ to $214\text{--}215^{\circ}/760$ mm.) by sulfonation, recrystallization of the barium sulfonate, and regeneration of the bromo compound by acid hydrolysis.

3. Methods of Preparation

The procedure given was developed by Ghigi ² from an earlier preparation by Jacobsen.³ 4-Bromo-*o*-xylene has also been prepared from 3,4-dimethylaniline by the Sandmeyer reaction.^{4, 5}

¹ *Org. Syntheses* Coll. Vol. 2, 4 (1943).

² Ghigi, *Ber.*, 71, 684 (1938).

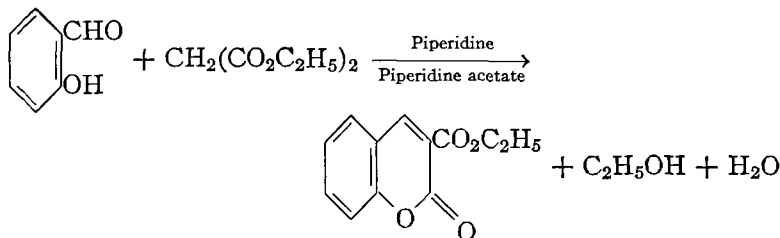
³ Jacobsen, *Ber.*, 17, 2372 (1884).

⁴ Brand, Ludwig, and Berlin, *J. prakt. Chem.*, [2] 110, 34 (1925).

⁵ Kohlrausch and Pongratz, *Monatsh.*, 64, 361 (1934).

3-CARBETHOXYCOUMARIN

(1,2-Benzopyran-3-carboxylic acid, 2-oxo-, ethyl ester)



Submitted by E. C. HORNING, M. G. HORNING, and D. A. DIMMIG.
 Checked by RICHARD T. ARNOLD and MARSHALL FREERKS.

1. Procedure

In a 500-ml. round-bottomed flask equipped with a reflux condenser are placed 61 g. (0.50 mole) of salicylaldehyde (Note 1), 88 g. (0.55 mole) of ethyl malonate, and 200 ml. of absolute ethanol. To this mixture are added 5 ml. of piperidine (Note 2) and 0.5 ml. of glacial acetic acid, and the solution is heated under reflux for 3 hours. The hot solution is transferred to a 1-l. Erlenmeyer flask, the reaction flask is rinsed with 20 ml. of ethanol, and the ethanol rinse and 330 ml. of hot water (Note 3) are added to the solution. The product crystallizes readily as the solution cools; the mixture is stirred from time to time as crystallization proceeds and is finally stored overnight in a refrigerator. The crystalline product is collected by filtration and washed with a solution made from 80 ml. of 95% ethanol and 120 ml. of water. The material is dried in the air. The yield is 85–91 g. (78–83%) of product melting at 91–93°.

The product may be recrystallized by dissolving it in 200 ml. of hot ethanol (95%), filtering, and adding 315 ml. of hot water. The recrystallized product is washed on the filter with 200 ml. of aqueous alcohol, as before, and air-dried. The yield of white 3-carbethoxycoumarin is 79–85 g. (73–78%); m.p. 92–94°.

2. Notes

1. The yield of the final product (m.p. 92–94°) may be increased to 80–84% by the use of salicylaldehyde purified in the following manner.

*Preparation of pure salicylaldehyde.*¹ Two hundred and fifty grams (1 mole) of copper sulfate pentahydrate is dissolved in 500 ml. of hot water in a 1-l. Erlenmeyer flask, and 244 g. (2 moles) of salicylaldehyde (Eastman Practical grade) is added. A solution of 80 g. (2 moles) of sodium hydroxide in 100 ml. of water is added slowly in small portions with intermittent vigorous shaking. The mixture is permitted to cool slowly to room temperature with intermittent shaking and is finally allowed to stand overnight. The solid is collected and washed with 200 ml. of ethanol (95%), digested with 400 ml. of ether, and again collected on a filter. Without drying, the product is treated with 1 l. of water containing 108.5 g. (59 ml., 1.05 moles) of 95% sulfuric acid. The mixture is shaken vigorously, and 200 ml. of ether is added to break up the oily mass that forms. The aldehyde is collected in ether and recovered by distillation of the dried (over calcium sulfate) solution. It distils at 96–97°/35 mm.; the recovery is 90%.

2. Eastman Practical grade is satisfactory.

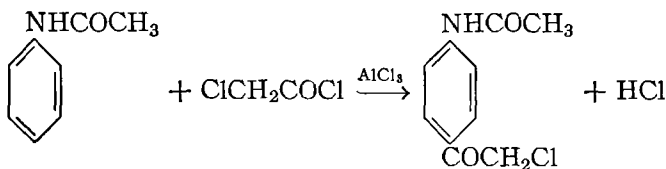
3. The water should be heated to about 60°.

3. Methods of Preparation

This compound has been prepared only by the Knoevenagel² condensation, with a secondary amine as a catalytic agent.

¹ Claisen and Eisleb, *Ann.*, **401**, 95 (1914).

² Knoevenagel, *Ber.*, **31**, 2593 (1898).

***p*-CHLOROACETYLACETANILIDE**(Acetanilide, *p*-chloroacetyl-)

Submitted by J. L. LEISERSON and A. WEISSBERGER.

Checked by CLIFF S. HAMILTON and YAO-HUA WU.

1. Procedure

Caution! Carbon disulfide, used as a solvent in this preparation, is highly inflammable; its vapor may ignite on contact with a hot laboratory steam line.

In a 5-l. three-necked flask mounted on a steam bath in the hood and equipped with a mechanical stirrer (Note 1) and a wide-bore condenser (Note 1) is placed 1.4 kg. (1.1 l.) of carbon disulfide. Through the open neck of the flask 202 g. (1.5 moles) of acetanilide and 300 g. (2.66 moles) of chloroacetyl chloride (Note 2) are introduced. The mixture is vigorously stirred while 600 g. (4.5 moles) of aluminum chloride is added in 25–50-g. portions over a period of 20–30 minutes; the neck of the flask is stoppered between additions (Note 3). After the addition of the last portion of aluminum chloride, the mixture is heated at reflux temperature for 30 minutes while stirring is continued. Heating and stirring are discontinued and the mixture is allowed to stand for 3 hours, during which time it separates into layers. The upper layer (carbon disulfide) is decanted, and the viscous red-brown lower layer is poured cautiously with stirring into about 1 kg. of finely crushed ice to which 100 ml. of concentrated hydrochloric acid has been added. After the hydrolysis of the aluminum chloride, the product crystallizes as a white solid, which is collected on a Büchner funnel and washed well with water. It is then trans-

ferred to a beaker where it is thoroughly washed by stirring with sufficient 95% ethanol to give a fluid slurry. The solid is again collected on the funnel. After drying in the air it melts at 213–214° and weighs 250–265 g. (79–83%). It can be recrystallized from 95% ethanol (about 1 l. of the solvent being required for 40 g. of the solid) as fine white crystals melting at 216°; the recovery in the recrystallization, without reworking of the mother liquor, is about 70%.

2. Notes

1. Unless a well-ventilated hood is available the stirrer should be provided with a seal and the condenser should be connected to a gas-absorption trap.

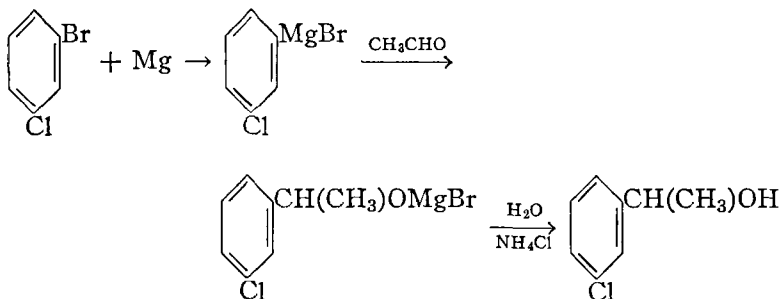
2. The chloroacetyl chloride should be weighed in the hood; it is strongly lachrymatory.

3. The addition of each portion of aluminum chloride causes vigorous boiling.

3. Methods of Preparation

The method of preparation given, devised by Kunckell,¹ is the only one reported.

¹ Kunckell, *Ber.*, **33**, 2644 (1900).

***m*-CHLOROPHENYLMETHYLCARBINOL**(Benzyl alcohol, *m*-chloro- α -methyl-)

Submitted by C. G. OVERBERGER, J. H. SAUNDERS, R. E. ALLEN, and ROBERT GANDER.

Checked by ARTHUR C. COPE and THEODORE T. FOSTER.

1. Procedure

A dry 2-l. three-necked round-bottomed flask is equipped with a sealed stirrer, a 500-ml. dropping funnel (Note 1), and an efficient reflux condenser attached to a calcium chloride tube. In the flask are placed 29.1 g. (1.2 gram atoms) of magnesium turnings, a crystal of iodine, and about 50 ml. of dry ether. A solution of 229 g. (1.2 moles) of *m*-bromochlorobenzene (Note 2) in 850 ml. of dry ether is added with stirring at a rate which maintains rapid refluxing. The reaction begins after 20–50 ml. of the ether solution is added (Note 3), and the addition requires 1–3 hours. The mixture is stirred and heated on the steam bath under reflux for 1 hour after all the *m*-bromochlorobenzene has been added.

A cooled solution of 60 g. (1.365 moles) of freshly distilled acetaldehyde in 200 ml. of dry ether (Note 4) is added through the dropping funnel during 2–3.5 hours, as rapidly as the condenser capacity permits. The mixture is stirred and heated under reflux for 1 hour after the addition is completed.

The reaction mixture is cooled in ice, and the addition compound is decomposed by adding dropwise with stirring 185 ml. of a 25% solution of ammonium chloride in water (Note 5). The ether solution becomes clear, and the salts separate as a cake. The ether solution is decanted, combined with 150 ml. of ether which has been used to rinse the salt cake, and dried over anhydrous magnesium sulfate. After removal of the ether the product is distilled under reduced pressure to give 154.5–164.5 g. (82.5–88%) of *m*-chlorophenylmethylcarbinol boiling at 99–104°/4 mm.; n_D^{25} 1.5405 (Note 6).

2. Notes

1. It is convenient to use a Hershberg stirrer with a rubber slip seal protected from ether vapor with a short water-cooled condenser. The dropping funnel may be connected to the flask through an extension tube to prevent clogging, which occurs if the Grignard reagent comes in contact with the acetaldehyde in the tip of the funnel.

2. *m*-Bromochlorobenzene was prepared according to the procedure described previously.¹ It may be purchased from the Eastman Kodak Company.

3. If the reaction does not begin spontaneously, the mixture should be heated under reflux until the reaction starts before more than 50 ml. of the *m*-bromochlorobenzene solution is added.

4. The solution is cooled to prevent loss of acetaldehyde by vaporization. Commercial acetaldehyde may be redistilled just before it is used, or acetaldehyde may be prepared by depolymerization of paraldehyde.²

5. The submitters state that the complex may be decomposed by pouring the reaction mixture onto 1 kg. of crushed ice to which 50 ml. of concentrated sulfuric acid has been added. The ether layer is separated, combined with two 100-ml. ether extracts of the aqueous layer, and washed with three 250-ml. portions of water, one 250-ml. portion of 10% sodium carbonate solution, and finally with 250 ml. of water.

6. The same general method (including the procedure of Note 5) has been used by the submitters to prepare the following substituted phenylmethylcarbinols:

CARBINOL	BOILING POINT	% YIELD
<i>m</i> -Trifluoromethylphenylmethylcarbinol	100–102°/17 mm.	83
<i>m</i> -Methylphenylmethylcarbinol	103–105°/6 mm.	71
<i>m</i> - <i>tert</i> .-Butylphenylmethylcarbinol	130–134°/17 mm.	56

An alternative preparation of similar carbinols, consisting in the reaction of methylmagnesium iodide with a substituted benzaldehyde, is advantageous when the aromatic aldehyde is available. The following carbinols have been prepared by the submitters in that way:

ALDEHYDE	CARBINOL	BOILING POINT	% YIELD
<i>p</i> -Chlorobenzaldehyde [Heyden Chemical Corporation; <i>Org. Syntheses</i> Coll. Vol. 2, 133 (1943)]	<i>p</i> -Chlorophenylmethylcarbinol	98–100°/4.5 mm.	59
<i>o</i> -Chlorobenzaldehyde (Heyden Chemical Corporation)	<i>o</i> -Chlorophenylmethylcarbinol	94°/4 mm.	69
<i>o</i> -Bromobenzaldehyde	<i>o</i> -Bromophenylmethylcarbinol	102–105°/2–3 mm.	73
<i>m</i> -Bromobenzaldehyde	<i>m</i> -Bromophenylmethylcarbinol	105–110°/2–3 mm.	74
<i>p</i> -Bromobenzaldehyde [<i>Org. Syntheses</i> Coll. Vol. 2, 89, 442 (1943)]	<i>p</i> -Bromophenylmethylcarbinol	90°/1 mm.	64
2,3-Dichlorobenzaldehyde	2,3-Dichlorophenylmethylcarbinol	112–113°/2 mm. m.p. 55–57°	76
2,4-Dichlorobenzaldehyde (Heyden Chemical Corporation)	2,4-Dichlorophenylmethylcarbinol	125–126°/7 mm.	62
2,6-Dichlorobenzaldehyde (Eastman Kodak Company)	2,6-Dichlorophenylmethylcarbinol	104–107°/2.5 mm.	89
3,5-Dichlorobenzaldehyde	3,5-Dichlorophenylmethylcarbinol	126°/4 mm.	69
3,4-Dichlorobenzaldehyde (Heyden Chemical Corporation)	3,4-Dichlorophenylmethylcarbinol	125–130°/3–4 mm.	73

3. Methods of Preparation

This procedure is adapted from the preparation described by Marvel and Schertz.³ *m*-Chlorophenylmethylcarbinol also has been prepared from *m*-chlorobenzaldehyde and methylmagnesium iodide.^{4, 5, 6}

¹ *Org. Syntheses*, **24**, 22 (1944).

² *Org. Syntheses Coll. Vol. 2*, 407 (1943).

³ Marvel and Schertz, *J. Am. Chem. Soc.*, **65**, 2054 (1943).

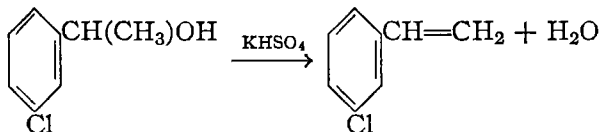
⁴ Lock and Bock, *Ber.*, **70**, 916 (1937).

⁵ Brooks, *J. Am. Chem. Soc.*, **66**, 1295 (1944).

⁶ Ushakov and Matuzov, *J. Gen. Chem. U.S.S.R.*, **14**, 120 (1944) [*C.A.*, **39**, 916 (1945)].

m-CHLOROSTYRENE

(Styrene, *m*-chloro-)



Submitted by C. G. OVERBERGER and J. H. SAUNDERS.

Checked by ARTHUR C. COPE and THEODORE T. FOSTER.

1. Procedure

A 500-ml. three-necked round-bottomed flask is attached to a 250-ml. dropping funnel and a total-condensation variable take-off fractionating column with a 20 by 1.2 cm. section packed with glass helices (Note 1). The fractionating column is fitted to a 500-ml. receiving flask. In the reaction flask are placed 12.5 g. of powdered fused potassium acid sulfate and 0.05 g. of *p*-*tert*.-butylcatechol. The flask is immersed in an oil bath maintained at 220–230°, and 145 g. (0.925 mole) of *m*-chlorophenylmethylcarbinol (p. 28) and 0.05 g. of *p*-*tert*.-butylcatechol (Note 2) are placed in the dropping funnel. The system is evacuated to a

pressure of 125 mm., maintained by a manostat, and the *m*-chlorophenylmethylcarbinol is added dropwise at a rate (15–20 drops per minute) which maintains a vapor temperature at 110–120° at the top of the column. The *m*-chlorostyrene and water formed are collected in a receiver. When the addition is completed (5.5–8.5 hours) the pressure is held constant until distillation stops, and it is then reduced to 20 mm. until no more liquid distills.

The distillate is rinsed into a separatory funnel with 25 ml. of ether, and the organic layer is separated and dried over 10 g. of anhydrous magnesium sulfate. The drying agent is separated and rinsed with 25 ml. of ether, and 0.1 g. of *p*-*tert*.-butylcatechol is added to the solution. The ether is removed, and the product is distilled under reduced pressure. *m*-Chlorostyrene is obtained in a yield of 102–106 g. (80–82.5%), boiling at 55–57°/3 mm.; n_D^{20} 1.5625 (Notes 3 and 4). A small amount (3–8 g.) of *m*-chlorophenylmethylcarbinol can be recovered as a higher-boiling fraction.

2. Notes

1. Effective separation of *m*-chlorostyrene from *m*-chlorophenylmethylcarbinol is possible with the short column specified. If a fractionating column is not used, lower conversions result and the crude product contains *m*-chlorophenylmethylcarbinol, which can be separated by fractional distillation and used in a subsequent preparation.

2. The submitters state that hydroquinone is not a satisfactory polymerization inhibitor for use in this preparation but that picric acid is very effective (less than 0.01 g. is required).

3. The submitters have used a similar procedure to prepare the following substituted styrenes from arylmethylcarbinols. The reactions were conducted more rapidly (addition rate about 2 drops per second), and no fractionating column was used in the initial distillation. A lower pressure (100 mm.) was used in dehydration of the dichlorophenylmethylcarbinols. The yields cited are based on the weights of arylmethylcarbinols which reacted

varying amounts of the carbinols were recovered in the distillation of the products.

	BOILING POINT	% YIELD
<i>o</i> -Chlorostyrene	67–69°/3–3.5 mm.	64–66.5
<i>p</i> -Chlorostyrene	65°/4 mm.	57
<i>o</i> -Bromostyrene	64–65°/3 mm.	64.5
<i>m</i> -Bromostyrene	74–75°/3 mm.	56
<i>p</i> -Bromostyrene	87–88°/12 mm.	50
<i>m</i> -Fluorostyrene	30–32°/2 mm.	45
2,3-Dichlorostyrene	92–94°/4–5 mm.	44
2,4-Dichlorostyrene	81°/6 mm.	33
3,4-Dichlorostyrene	95°/5 mm.	63.5
2,6-Dichlorostyrene	64–65°/3 mm.	31.5
3,5-Dichlorostyrene	59°/1 mm.	43.5

The dehydration procedure of this preparation is stated to be unsatisfactory for substituted phenylmethylcarbinols which have a strongly electronegative group, such as the nitro or trifluoromethyl group, in the *meta* position.

4. Some color due to small amounts of iodine may be present in substituted styrenes prepared by this procedure from arylmethylcarbinols synthesized from the corresponding aldehyde and methylmagnesium iodide. If present, iodine may be removed by shaking the crude product with 1 g. of powdered zinc and 25 ml. of water.

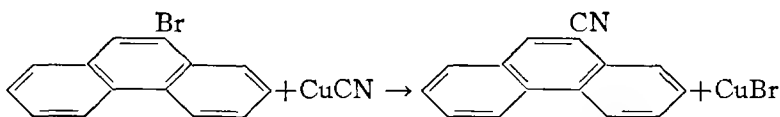
3. Methods of Preparation

m-Chlorostyrene has been prepared by dehydration of *m*-chlorophenylmethylcarbinol by modifications of this procedure.^{1,2,3}

¹ Marvel and Schertz, *J. Am. Chem. Soc.*, **65**, 2054 (1943).

² Brooks, *J. Am. Chem. Soc.*, **66**, 1295 (1944).

³ Ushakov and Matuzov, *J. Gen. Chem. U.S.S.R.*, **14**, 120 (1944) [*C.A.*, **39**, 916 (1945)].

9-CYANOPHENANTHRENE**(9-Phenanthrenecarbonitrile)**

Submitted by JOSEPH E. CALLEN, CLINTON A. DORN-FELD, and GEORGE H. COLEMAN.¹

Checked by ROBERT E. CARNAHAN and HOMER ADKINS.

1. Procedure

In a 2-l. Claisen flask (Note 1) are mixed 1 kg. (3.90 moles) of 9-bromophenanthrene (p. 19) (Note 2) and 400 g. (4.46 moles) of cuprous cyanide. A small motor-driven spiral stirrer is inserted, and the flask is heated (Note 3) at 260° for 6 hours (Note 4). The flask is then provided with a fine capillary inlet tube, a thermometer, and a 2-l. distilling flask attached to the side arm of the Claisen flask as receiver. The 9-cyanophenanthrene is distilled at 190–195°/2 mm. The yield of crude product is 740 g. (93%), m.p. 94–98°. One recrystallization from about 2 l. of dry ethanol yields 690 g. (87%) of material melting at 105–107° (Notes 5 and 6).

2. Notes

1. It is necessary to sacrifice the flask after the distillation, since the inorganic residue cannot be removed easily.

2. The 9-bromophenanthrene need not be recrystallized if it has been purified by distillation.

3. The heating may be readily controlled by the use of an electric heating mantle and variable transformer.

4. Increasing the heating period beyond 6 hours has no effect on the yield.

5. The melting point can be raised to 110° by further recrystallization from ethanol. The unrecrystallized product is probably pure enough for most purposes.

6. The checkers operated on one-tenth the scale and duplicated the percentage yields obtained on the larger scale. Material melting at 109–110° was obtained in a 75–77% yield.

3. Methods of Preparation

The procedure described above is an adaptation of methods of Mosettig and van de Kamp² and of Bachmann and Boatner.³ 9-Cyanophenanthrene has also been prepared from 9-phenanthrenesulfonic acid⁴ and from phenanthrene-9-aldoxime.⁵

¹ Work done under contract with the Office of Scientific Research and Development.

² Mosettig and van de Kamp, *J. Am. Chem. Soc.*, **54**, 3355 (1932).

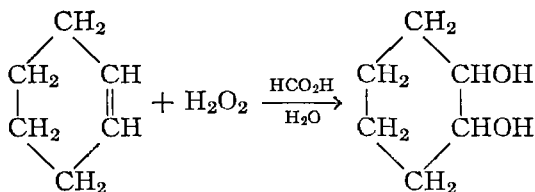
³ Bachmann and Boatner, *J. Am. Chem. Soc.*, **58**, 2098 (1936); Goldberg, Ordas, and Carsh, *J. Am. Chem. Soc.*, **69**, 260 (1947).

⁴ Werner and Kunz, *Ann.*, **321**, 327 (1902).

⁵ Shoppee, *J. Chem. Soc.*, **1933**, 40.

trans-1,2-CYCLOHEXANEDIOL

(1,2-Cyclohexanediol, *trans*-)



Submitted by ALAN ROEBUCK and HOMER ADKINS.

Checked by ARTHUR C. COPE and CLAUDE F. SPENCER.

1. Procedure

One hundred and forty milliliters of 30% hydrogen peroxide (1.4 moles) (Note 1) is added to 600 ml. of 88% formic acid (13.7 moles) (Note 2) in a 1-l. three-necked flask equipped with a thermometer and a motor-driven stirrer. Freshly distilled cyclohexene (82 g., 1.0 mole) (Note 3) is added slowly from a dropping

funnel over a period of 20–30 minutes while the temperature of the reaction mixture is maintained between 40° and 45° by cooling with an ice bath and by controlling the rate of addition (Note 4). The reaction mixture is kept at 40° for 1 hour after all the cyclohexene has been added, and then it is allowed to stand overnight at room temperature.

The formic acid and water are removed by distillation from a steam bath under reduced pressure. An ice-cold solution of 80 g. of sodium hydroxide in 150 ml. of water is added in small portions to the residual viscous mixture of the diol and its formates, with care that the temperature of the mixture does not exceed 45°. The alkaline solution is warmed to 45°, and an equal volume (350 ml.) or more of ethyl acetate is added. After thorough extraction, the lower layer is separated and extracted at 45° six times with equal volumes of ethyl acetate. The seven ethyl acetate solutions (Note 5) are combined (total volume about 2.1 l.), and the solvent is distilled from a steam bath until the residual volume is 300–350 ml. and the solid product begins to crystallize. The mixture is cooled to 0°, and the product is separated by filtration (77–90 g., melting in the range of 90–98°). The mother liquor is concentrated on a steam bath to a volume of 65–75 ml., and more solid crystallizes. The mixture is cooled and filtered as before and yields an additional 4–15 g. of crude product melting in the range of 80–89°. *trans*-1,2-Cyclohexanediol, b.p. 120–125°/4 mm., is obtained by distillation of the combined crude products, with the use of an oil bath and a flask having a side arm and an air condenser sufficiently wide that they will not become plugged as the product solidifies (Note 6). The yield of product of m.p. 101.5–103° is 75–85 g. (65–73%) (Note 7).

2. Notes

1. The concentration of the hydrogen peroxide may be determined by titration with 0.2 *N* potassium permanganate in acid solution.

2. Less formic acid than is specified may be used, but the yields are lower and the reaction is not so easily controlled.

3. The cyclohexene used may be the commercial product or it may be prepared from cyclohexanol.¹

4. If the temperature rises above 45°, the reaction may be stopped by discontinuing the stirring.

5. The total quantity of ethyl acetate required is less if the first three extractions are combined and the solvent required for successive extractions is distilled at a steam bath from this solution.

6. If there is an appreciable quantity of solid residue in the flask, it may be dissolved in hot water and crystallized by cooling in ice. The crystals of cyclohexanediol, after being dried, may be distilled as described above.

7. The product can be recrystallized from ethyl acetate.

3. Methods of Preparation

The method described is essentially that of Swern, Billen, Findley, and Scanlan.² *trans*-1,2-Cyclohexanediol also has been prepared by hydrolysis³ of cyclohexene oxide. *cis*-1,2-Cyclohexanediol has been prepared by the reaction of cyclohexene with hydrogen peroxide in tertiary butyl alcohol with osmium tetroxide as a catalyst.⁴ Hydrogenation of catechol over Raney nickel catalyst at 150° gives a mixture (m.p. 73–77°) of *cis*- and *trans*-1,2-cyclohexanediols.⁵

¹ *Org. Syntheses* Coll. Vol. 1, 183 (1941).

² Swern, Billen, Findley, and Scanlan, *J. Am. Chem. Soc.*, **67**, 1786 (1945).

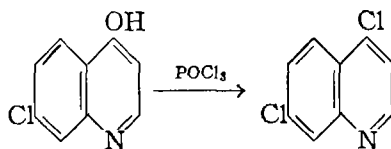
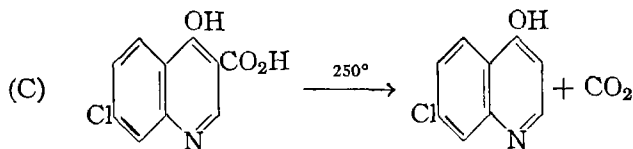
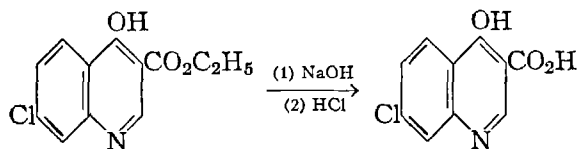
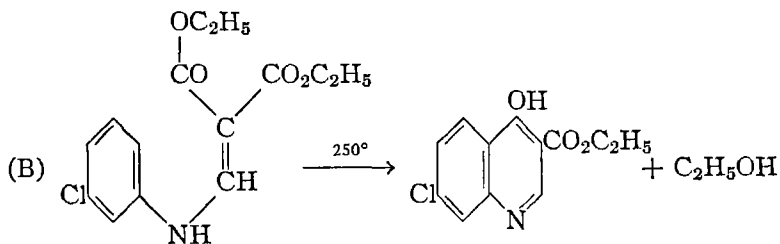
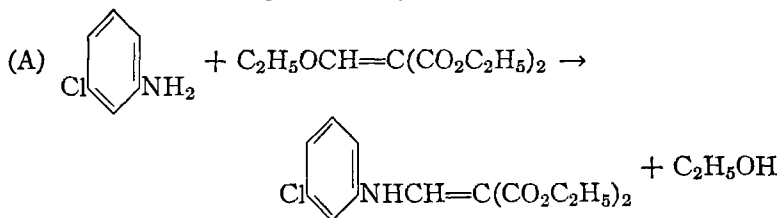
³ Criegee and Stanger, *Ber.*, **69**, 2753 (1936).

⁴ Milas and Sussman, *J. Am. Chem. Soc.*, **59**, 2345 (1937).

⁵ Donald Robinson, Ph.D. Thesis, University of Wisconsin, 1948.

4,7-DICHLOROQUINOLINE

(Quinoline, 4,7-dichloro-)

Submitted by CHARLES C. PRICE and ROYSTON M. ROBERTS.¹

Checked by J. R. ROLAND and R. S. SCHREIBER.

1. Procedure

A. *Ethyl α -carbethoxy- β -*m*-chloroanilinoacrylate*. A few boiling chips are added to a mixture of 127.5 g. (1.0 mole) of *m*-chloroaniline (Note 1) and 233 g. (1.1 moles) of ethyl ethoxymethylenemalonate (p. 60) (Note 2) in an open 500-ml. round-bottomed flask. The mixture is heated on a steam bath for 1 hour, the evolved ethanol being allowed to escape. The warm product is used directly in the next step (Note 3).

B. *7-Chloro-4-hydroxy-3-quinolinecarboxylic acid*. In a 5-l. round-bottomed flask equipped with an air condenser 1 l. of Dowtherm A (Note 4) is heated to vigorous boiling, and the product of the above step is poured in through the condenser. Heating is continued for 1 hour, during which time a large proportion of the cyclization product crystallizes. The mixture is cooled, filtered, and washed with two 400-ml. portions of Skellysolve B (b.p. 61–70°) to remove the major portion of colored impurities. The air-dried filter cake (Note 5) is mixed with 1 l. of 10% aqueous sodium hydroxide, and the mixture is refluxed vigorously until all the solid ester dissolves (about 1 hour). The saponification mixture is cooled, and the aqueous solution is separated from any oil that may be present. The solution is acidified to Congo red paper with concentrated hydrochloric acid (ca. 270 ml. of the 38% acid, sp. gr. 1.19) or 10% sulfuric acid. The 7-chloro-4-hydroxy-3-quinolinecarboxylic acid, weight 190–220 g. (85–98%), is collected by filtration and washed thoroughly with water. The dry acid melts at about 266° with effervescence (Note 6).

C. *7-Chloro-4-quinolinol and 4,7-dichloroquinoline*. The above air-dried acid (Note 7) is suspended in 1 l. of Dowtherm A in a 2-l. flask equipped with a stirrer and a reflux condenser. The mixture is boiled for 1 hour under a stream of nitrogen to assist in the removal of the water (Note 8). The clear, light-brown solution is cooled to room temperature, and 90 ml. (150 g., 0.98 mole) of phosphorus oxychloride is added. The temperature is raised to 135–140°, and the mixture is stirred for 1 hour. The reaction mixture is cooled and poured into a separatory funnel. The portion of the mixture adhering to the flask is rinsed into

the funnel with ether, and the solution is washed with three 500-ml. portions of 10% hydrochloric acid. The combined acid extracts are cooled in ice and neutralized with 10% sodium hydroxide to precipitate the 4,7-dichloroquinoline. The solid is collected, washed thoroughly with water, and dried; it weighs 130–145 g. (66–73%) and melts at 80–82°. The pure product is obtained by one recrystallization from Skellysolve B (b.p. 61–70°); weight 110–120 g. (55–60%), m.p. 84–85°.

2. Notes

1. The checkers found it desirable to distil the *m*-chloroaniline through a 20-plate column, the fraction boiling at 64–66°/18 mm. being collected for use in this preparation.

2. A good criterion of the purity of the ethyl ethoxymethylenemalonate is the refractive index; material of $n_D^{20} > 1.4600$ is satisfactory. The checkers redistilled the ethyl ethoxymethylenemalonate through a 1 by 12 in. bead-packed column just before use and employed the fraction boiling at 112–115°/0.1 mm., n_D^{25} 1.4604.

3. The anilinoacrylate can be recrystallized from low-boiling petroleum ether as slender white needles, m.p. 55–56°.

4. Dowtherm A, a mixture of biphenyl and diphenyl ether, may be replaced by diphenyl ether. The high-boiling solvent is most conveniently heated to its boiling point (ca. 250°) by an electric heating mantle.

5. The yield of ester isolated at this point is 215–240 g. (85–95%), m.p. 295–297°.

6. The acid can be recrystallized from ethanol as fine white needles melting with decomposition at 273–274°.

7. The acid need not be dry if care is taken to remove water during the decarboxylation in boiling Dowtherm.

8. If the 7-chloro-4-quinolinol is desired, it is more convenient to effect the decarboxylation without a solvent.²

3. Methods of Preparation

4,7-Dichloroquinoline has been prepared through a somewhat similar scheme from *m*-chloroaniline and oxaloacetic ester³ or formylacetic ester.⁴ The synthesis outlined above can be modified in various ways.^{2, 5, 6, 7}

The procedure has been utilized on a large scale in the preparation of several thousand pounds of 4,7-dichloroquinoline, essentially as described above. It has also been applied successfully to many other aromatic amines, including aniline,⁸ *o*-,⁹ *m*-,⁹ and *p*-anisidine,³ 3,4-dimethylaniline,³ *o*-nitroaniline,⁸ *p*-chloroaniline,⁸ *m*- and *p*-phenoxyaniline,⁸ *p*-dimethylaminoaniline,⁸ 3,4-dimethoxyaniline,⁸ 3-aminopyridine,³ *o*-phenylenediamine,¹⁰ and 8-aminoquinoline.¹⁰

¹ Work done under contract with the Office of Scientific Research and Development.

² Price and Roberts, *J. Am. Chem. Soc.*, **68**, 1206 (1946).

³ Surrey and Hammer, *J. Am. Chem. Soc.*, **68**, 115 (1946).

⁴ Price, Leonard, and Reitsema, *J. Am. Chem. Soc.*, **68**, 1256 (1946).

⁵ Snyder and Jones, *J. Am. Chem. Soc.*, **68**, 1253 (1946).

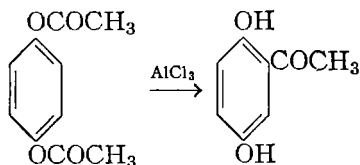
⁶ Price and Roberts, *J. Am. Chem. Soc.*, **68**, 1255 (1946).

⁷ Price, Leonard, and Herbrandson, *J. Am. Chem. Soc.*, **68**, 1251 (1946).

⁸ Riegel, Lappin, Adelson, Jackson, Albisetti, Dodson, and Baker, *J. Am. Chem. Soc.*, **68**, 1264 (1946).

⁹ Lauer, Arnold, Tiffany, and Tinker, *J. Am. Chem. Soc.*, **68**, 1268 (1946).

¹⁰ Snyder and Freier, *J. Am. Chem. Soc.*, **68**, 1320 (1946).

2,5-DIHYDROXYACETOPHENONE**(Acetophenone, 2,5-dihydroxy-; quinacetophenone)**

Submitted by G. C. AMIN and N. M. SHAH.

Checked by R. S. SCHREIBER and W. W. PRICHARD.

1. Procedure

A mixture of 50 g. (0.257 mole) of dry hydroquinone diacetate (p. 68) and 116 g. (0.87 mole) (Note 1) of anhydrous aluminum chloride is finely powdered in a mortar and introduced into a dry 500-ml. round-bottomed flask fitted with an air condenser protected by a calcium chloride tube and connected to a gas-absorption trap.¹ The flask is placed in an oil bath (Note 2) which is heated slowly from room temperature so that at the end of about $\frac{1}{2}$ hour the temperature of the oil reaches $110\text{--}120^\circ$, at which point the evolution of hydrogen chloride begins. The temperature is then raised slowly to $160\text{--}165^\circ$ and maintained at that point for about 3 hours (Note 3); at the end of about 2 hours the evolution of hydrogen chloride becomes very slow and the mass assumes a green color and becomes pasty in consistency (Note 4).

The flask is removed from the oil bath and allowed to cool to room temperature. The excess aluminum chloride is decomposed by treating the reaction mixture with 350 g. of crushed ice followed by 25 ml. of concentrated hydrochloric acid. The solid obtained is collected on a Büchner funnel and washed with two 100-ml. portions of cold water. The crude product weighs about 35 g. (89–90%). Recrystallization from 4 l. of water yields 25–30 g. (64–77%) of green, silky needles melting at $202\text{--}203^\circ$ (Note 5).

2. Notes

1. Ordinary commercial aluminum chloride can be used. If the amount of this reagent is less than 3 moles per mole of the ester the yield diminishes. To compensate for any inert ingredients in the commercial aluminum chloride, the reagent is employed in an excess of about 10% over 3 moles.

2. The flask should not touch the bottom of the oil bath; if it does, the lower portion of the mixture may char.

3. If the evolution of the hydrogen chloride becomes vigorous, the calcium chloride tube may be removed temporarily and the top of the condenser connected directly to the gas-absorption trap. When the gas evolution slackens and there is no longer any danger that the calcium chloride tube will be blown off, the guard tube is reinserted.

4. The reaction requires about 2 hours, but the heating is continued another hour to ensure its completion.

5. The product may be recrystallized from 250 ml. of 95% ethanol rather than from the much larger quantity of water.

3. Methods of Preparation

2,5-Dihydroxyacetophenone has been prepared in 54% yield ² by heating hydroquinone diacetate, hydroquinone, and anhydrous aluminum chloride. It has also been prepared ³ by the reaction of hydroquinone with acetic acid in the presence of zinc chloride.

The procedure given has also been applied in the Fries rearrangement of hydroquinone dipropionate, with the production of 2,5-dihydroxypropiofenone in good yields.

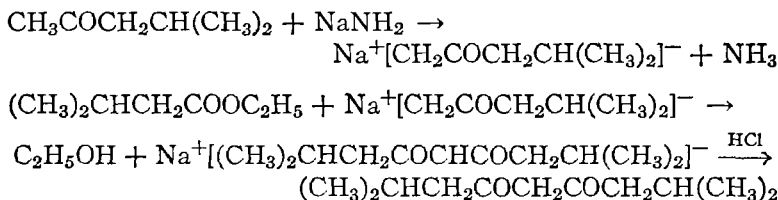
¹ *Org. Syntheses* Coll. Vol. 2, 4 (1943).

² Rosenmund and Lohfert, *Ber.*, **61**, 2606 (1928).

³ Nencki and Schmid, *J. prakt. Chem.*, **23**, 546 (1881).

DIISOVALERYLMETHANE

(4,6-Nonanedione, 2,8-dimethyl-)



Submitted by C. R. HAUSER, J. T. ADAMS, and R. LEVINE.

Checked by ARTHUR C. COPE and FRANK S. FAWCETT.

1. Procedure

Approximately 300 ml. of commercial anhydrous liquid ammonia is added to a 500-ml. three-necked round-bottomed flask equipped with a mercury-sealed stirrer and a reflux condenser connected to a soda-lime drying tube (Note 1). The drying tube is attached to a gas-absorption trap, or the apparatus is assembled in a well-ventilated hood. The third neck of the flask is closed with a stopper. Freshly cut sodium (13.8 g., 0.6 gram atom) is weighed under xylene or kerosene, and a small amount is added to the liquid ammonia, with stirring, until a permanent blue color is produced. A few small crystals of ferric nitrate are added to catalyze the conversion of sodium to sodium amide (Note 2), and when the blue color has disappeared the remainder of the sodium is added in small pieces. When the sodium is converted completely to sodium amide, as indicated by change of the blue solution to a gray suspension, the ammonia is evaporated by warming the flask on a steam bath. During this operation sufficient dry ether is added through a dropping funnel (attached to the third neck of the flask) so that the volume of the liquid remains approximately 300 ml. After practically all the ammonia has been evaporated, as indicated by refluxing of the ether, the sodium amide suspension is stirred and heated under reflux for

a few minutes and then cooled to room temperature. The procedure to this point requires approximately 1 hour.

A solution of 30 g. (0.3 mole) of redistilled methyl isobutyl ketone in 50 ml. of absolute ether is added to the stirred suspension of sodium amide during 5 to 10 minutes. After an additional 5 minutes, a solution of 78 g. (0.6 mole) of redistilled ethyl isovalerate in 50 ml. of dry ether is added during about 15 minutes. Stirring is continued for 2 hours while the mixture is heated under reflux on the steam bath. The gelatinous suspension of the sodium salt of diisovalerylmethane is poured into 300 ml. of water, made neutral to litmus by dilute hydrochloric acid, and extracted with three 100-ml. portions of ether. The solvent is removed by distillation under reduced pressure, and the residue is dissolved in an equal volume of methanol. A solution prepared from 44 g. of cupric acetate monohydrate and 350 ml. of water is heated nearly to the boiling point, filtered, and added to the methanol solution. The resulting mixture is allowed to stand until it has cooled to room temperature. The blue copper salt of diisovalerylmethane is collected on a Büchner funnel, pressed as dry as possible, washed on the funnel with 100 ml. of petroleum ether (b.p. 30–60°), and again sucked dry. The yield of the copper salt after air drying is 44–51 g. (69–79%); it melts in the range 150–155° (Note 3).

The diisovalerylmethane is regenerated by shaking the copper salt vigorously with 500 ml. of 10% sulfuric acid and 200 ml. of ether until all the salt has dissolved. The aqueous acid layer is extracted with two 100-ml. portions of ether, and the combined ether solutions are dried over anhydrous sodium sulfate. The solvent is removed, and the residue is distilled under reduced pressure. The yield of diisovalerylmethane is 32–42 g. (58–76%, based on methyl isobutyl ketone), b.p. 115–116°/20 mm., n_D^{25} 1.4565 (Notes 4 and 5).

2. Notes

1. Apparatus fitted with standard-taper ground-glass joints is convenient for this preparation.
2. It may be helpful to provide additional catalysis of the con-

version to sodium amide of the small amount of sodium added initially by bubbling dry air through the solution.¹

3. After recrystallization from methanol or 95% ethanol the fluffy light blue copper salt melts at 157–158°.

4. The submitters state that the reaction may be conducted with equal success by using 0.6 mole each of sodium amide and methyl isobutyl ketone, and 0.3 mole of ethyl isovalerate (yield 75% based on the ester).^{2,3}

5. Acetone may be acylated with ethyl laurate by either procedure (with excess ester or excess ketone). Lauroylacetone (m.p. 31.5–32°) is obtained in 75% yield³ by either procedure.

3. Methods of Preparation

Diisovaleryl methane has been prepared only by the method described.^{2,3}

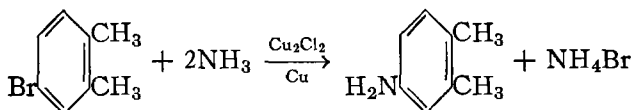
¹ Leffler, *Organic Reactions*, **1**, 99, John Wiley & Sons, New York, 1942; Vaughn, Vogt, and Nieuwland, *J. Am. Chem. Soc.*, **56**, 2120 (1934).

² Adams and Hauser, *J. Am. Chem. Soc.*, **66**, 1220 (1944).

³ Levine, Conroy, Adams, and Hauser, *J. Am. Chem. Soc.*, **67**, 1510 (1945).

3,4-DIMETHYLANILINE

(Xylidine, 3,4-)



Submitted by W. A. WISANSKY and S. ANSBACHER.

Checked by N. L. DRAKE, WILKINS REEVE, and JOHN STERLING, JR.

1. Procedure

In a 1.1-l. steel reaction vessel (Note 1) are placed 200 g. (1.08 moles) of 4-bromo-*o*-xylene (p. 22), 14 g. copper wire, and 600 ml. (540 g., 9.0 moles) of 28% ammonia containing 12 g. of cuprous chloride. The steel reaction vessel is heated and rocked at 195°

(thermostatic control) (Note 2) for 14 hours (Note 3); the pressure rises to 700–1000 lb. After cooling, the bomb is emptied, and the two layers are separated; 40 ml. of 40% sodium hydroxide is added to the organic layer, and the mixture is steam-distilled. The amine distills and crystallizes when the distillate is cooled. It is separated from the water and dissolved in 500 ml. of 8% hydrochloric acid; the acid solution is extracted with two 100-ml. portions of ether (Note 4). The ether extracts are discarded, and the acid solution is made alkaline with 160 ml. of 40% sodium hydroxide. The resulting mixture is steam-distilled (Note 5). The distillate is cooled, most of the water is decanted, and the crystalline xylidine is dissolved by shaking with two 250-ml. portions of ether. The combined ether solutions are dried over calcium chloride and concentrated by distillation at a steam bath. The residue is distilled under reduced pressure from a Claisen flask. The yield of 3,4-dimethylaniline, boiling at 116–118°/22–25 mm., is 103 g. (79%). This crude product is recrystallized from 200 ml. of petroleum ether (b.p. 60–80°); the hot solution is placed in a refrigerator, and the crystallization is allowed to proceed overnight. The yield of recrystallized 3,4-dimethylaniline is 86 g. (66%) (Note 6); it melts at 47.3–49.2° (Note 7).

2. Notes

1. A hydrogenation vessel supplied by the American Instrument Company is satisfactory. A certain amount of copper plates out on the walls of the bomb during the reaction, but most of it is removed when the apparatus is cleaned.

2. The heating and rocking are carried out in a hydrogenation assembly. The temperature must not be allowed to exceed 200°; at higher temperatures decomposition occurs and the yield suffers.

3. The optimum reaction time may vary slightly with apparatus of different types.

4. The crude product contains a small amount of unchanged 4-bromo-*o*-xylene which is removed by the ether extraction.

5. Caution must be exercised because a considerable amount of ether is present; it distills first and may be only partially con-

densed. A preliminary heating of the mixture on a steam bath does not remove the ether completely.

6. In an alternative method of purification the submitters collected the amine from the second steam distillation on a suction filter, pressed out the oily materials on the filter, and distilled the resulting crystalline product under diminished pressure; the distillate was not recrystallized. The checkers found it difficult to effect complete removal of oils by filtration; they preferred to omit this step and to recrystallize the distilled amine.

7. The reported melting point of 3,4-dimethylaniline varies from 47–48°¹ to 48.5–49°.²

3. Methods of Preparation

3,4-Dimethylaniline has been prepared by reduction of the corresponding nitro compound, either chemically^{2,3} or catalytically.⁴ It has been prepared from 3,4-dimethylphenol by heating with ammonia, ammonium bromide, and zinc bromide;⁵ from *m*-toluidine hydrochloride by alkylation with methanol at high temperatures;^{1,6} from anhydro-4-amino-2-methylbenzyl alcohol by dry distillation from calcium hydroxide;⁷ from 2-methyl-5-aminobenzyl alcohol by reduction with sodium; from 2-methyl-5-nitrobenzyl chloride and 2-methyl-5-nitrobenzyl acetate by catalytic reduction;⁸ from *o*-xylene by direct amination with hydroxylamine hydrochloride in the presence of aluminum chloride;⁹ and from 3,4-dimethylacetophenone by the Beckmann rearrangement of the oxime.¹⁰ The present method has been published.¹¹

¹ Limpach, *Ber.*, **21**, 643 (1888).

² Bamberger and Blangey, *Ann.*, **384**, 318 (1911).

³ Jacobsen, *Ber.*, **17**, 159 (1884).

⁴ Karrer, Becker, Benz, Frei, Salomon, and Schöpp, *Helv. Chim. Acta*, **18**, 1435 (1935).

⁵ Müller, *Ber.*, **20**, 1039 (1887).

⁶ Cripps and Hey, *J. Chem. Soc.*, **1943**, 14.

⁷ Barclay, Burawoy, and Thomson, *J. Chem. Soc.*, **1944**, 109.

⁸ Weinmayr, U. S. pat. 2,373,438 [*C.A.*, **39**, 3793 (1945)].

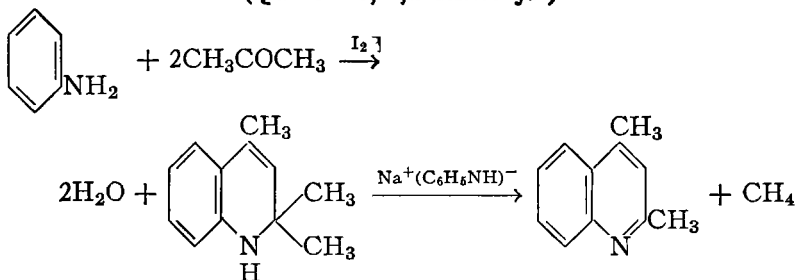
⁹ Graebe, *Ber.*, **34**, 1780 (1901).

¹⁰ Zaugg, *J. Am. Chem. Soc.*, **67**, 1861 (1945).

¹¹ Wisansky and Ansbacher, *J. Am. Chem. Soc.*, **63**, 2532 (1941).

2,4-DIMETHYLQUINOLINE

(Quinoline, 2,4-dimethyl-)

Submitted by W. R. VAUGHAN.¹

Checked by RICHARD T. ARNOLD and HORACE R. DAVIS, JR.

1. Procedure

A. "*Acetone-anil*" (Note 1). A mixture of 279 g. (3 moles) of aniline and 9 g. of iodine is placed in a 1-l. three-necked round-bottomed flask. The flask is fitted with a dropping funnel (the delivery tube of which extends below the liquid surface), a mercury-sealed stirrer (Note 2), and an adapter carrying a thermometer which extends into the liquid and a condenser system such that most of the aniline will return and all the water produced (as well as excess acetone) will distil (Note 3). The flask is now heated in an oil bath (Notes 4 and 5), and the reaction mixture is maintained at 170–175° while acetone is passed in through the dropping funnel at such a rate that no more than 2 drops of liquid distils per second. During the addition the mixture is vigorously stirred. A total volume of 850 ml. (670 g., 11.6 moles) of acetone is added over a 4-hour period, and about 610 ml. of distillate is collected. At the end of this period the reaction mixture is cooled and distilled in vacuum, three fractions being collected (up to 136°/15 mm., 136–141°/15 mm., and 141–146°/15 mm.). The acetone-water distillate is now distilled through a simple column at atmospheric pressure until essentially all the acetone has come over. There remains a mixture of oil and water which is sepa-

rated after being cooled. The oil is then used as the first fraction for a fractional distillation in vacuum of the reaction product, each of the previous fractions being added in succession. Three new fractions are collected: 78–82°/13 mm. (a little aniline); 82–133°/13 mm. (a small intermediate fraction); and 133–138°/13 mm. (acetone-anil). An appreciable quantity of tarry residue remains in the distillation flask. The yield based upon aniline actually consumed in the reaction is 61–68% (Note 5).

B. *2,4-Dimethylquinoline*. A small quantity of copper powder (Note 6) is added to 4.6 g. (0.2 gram atom) of sodium metal (small pieces) and 56 g. (0.6 mole) of dry aniline (Note 7) contained in a 1-l. round-bottomed flask. The mixture is warmed carefully over a low flame until the evolution of hydrogen ceases, at which time the mixture is usually black. A few boiling chips and 346 g. (2 moles) of acetone-anil are then added. The resulting mixture is heated at the reflux temperature (220–230°) until the evolution of gas (methane) ceases (Note 8). At the end of the reaction the mixture is cooled and then distilled in vacuum. The fraction boiling at 135–140°/12 mm. weighs 252–283 g. (80–90%) (Note 9).

2. Notes

1. The so-called acetone-anil has been assigned the structure indicated in accordance with the work of Craig.²

2. A convenient stirrer may be made from tantalum wire as described by Hershberg.³

3. A Liebig condenser in reflux position is heated with steam and connected at the top to a water-cooled downward condenser.

4. For a reaction temperature of 170–175° the oil is best maintained at about 200° during the addition of the acetone.

5. The reaction may be carried out at any temperature from 70° to 175°. At lower temperatures it is much slower and is best carried out by refluxing the theoretical quantities of acetone and aniline with iodine catalyst for an extended time. Regardless of the time or reaction temperature, if due allowance is made for aniline reclaimed at the end of the reaction the yield falls between the limits indicated. At the higher temperature, equilibrium is

attained more rapidly, as would be expected, and relatively little aniline is recovered. (A typical run may yield 40 g. of aniline and 297 g. of "anil," with 11 g. of middle fraction.)

6. The exact amount of copper powder used as a catalyst in the preparation of the sodium salt of aniline is not important. Approximately 0.2 g. has been found to be satisfactory in runs of the size described.

7. Aniline which has been recently distilled is satisfactory. An excess of aniline over the sodium is used to minimize decomposition of the 2,4-dimethylquinoline.²

8. The time required for the decomposition of the acetone-anil varies from 3 to 6 hours. The checkers, however, found that essentially all the methane is eliminated after 2 hours.

9. Fractionation of 245 g. of this product through a 14-plate Lecky-Ewell⁴ column yielded 6 g. of aniline, 3 g. of an intermediate fraction, and 218 g. (89%) of 2,4-dimethylquinoline, b.p. 149–150°/20 mm. (controlled). If the material is to be nitrated, the crude product is quite satisfactory.

3. Methods of Preparation

The present procedure for the preparation of acetone-anil is described by Reddelien.⁵ A reaction at lower temperature is reported by Craig,² who also describes the alkaline decomposition of the anil to 2,4-dimethylquinoline and methane and gives a method of purification of the final product. Other methods for the preparation of 2,4-dimethylquinoline involve the Beyer⁶ synthesis from aniline hydrochloride and ethylidene acetone, a modification of this synthesis,⁷ or the Combes⁸ synthesis from acetylacetone and aniline.

¹ Work done under contract with the Office of Scientific Research and Development.

² Craig, *J. Am. Chem. Soc.*, **60**, 1458 (1938).

³ Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).

⁴ Lecky and Ewell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 544 (1940).

⁵ Reddelien and Thurm, *Ber.*, **65**, 1511 (1932).

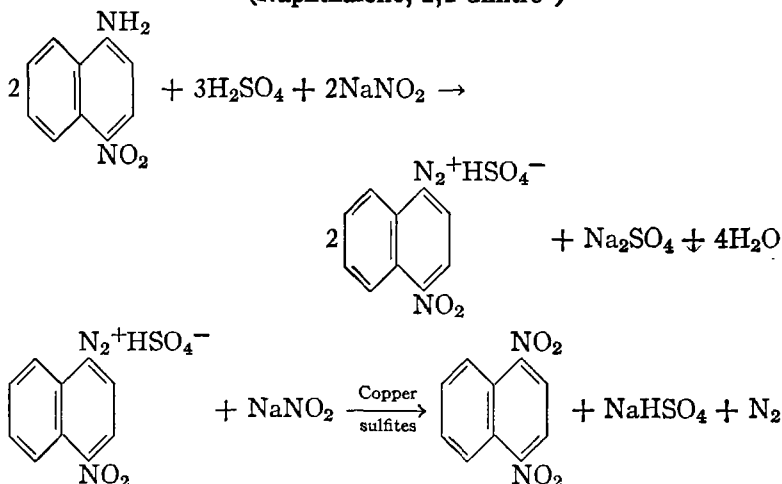
⁶ Beyer, *J. prakt. Chem.*, [2] **33**, 401 (1886).

⁷ Mikeska, Stewart, and Wise, *Ind. Eng. Chem.*, **11**, 456 (1919).

⁸ Combes, *Bull. soc. chim. France*, **49**, 89 (1888).

1,4-DINITRONAPHTHALENE

(Naphthalene, 1,4-dinitro-)



Submitted by H. H. HODGSON, A. P. MAHADEVAN, and E. R. WARD.

Checked by C. C. PRICE and SING-TUH VOONG.

1. Procedure

Ten grams (0.14 mole) of powdered sodium nitrite is dissolved in 50 ml. of concentrated sulfuric acid (sp. gr. 1.84) contained in a 1-l. beaker placed in an ice bath. A solution of 10 g. of 4-nitro-1-naphthylamine (0.053 mole) (p. 80) in 100 ml. of glacial acetic acid is prepared by heating, and the well-stirred solution is cooled to below 20°. Some crystals separate. The resulting thin slurry is dropped slowly into the cold solution of nitrosylsulfuric acid with mechanical stirring. Throughout the addition, and for 30 minutes thereafter, the temperature is kept below 20°. Seven hundred milliliters of dry ether is added slowly with stirring, and the temperature of the mixture is kept at 0° for 1 hour. At the end of this period, the precipitation (aided by scratching) of the crystalline 4-nitronaphthalene-1-diazonium sulfate is complete (Note 1). This precipitate is collected, washed with ether and

then with 95% ethanol until all the acid is removed, and finally dissolved in 100 ml. of iced water.

A saturated aqueous solution containing 50 g. of crystalline copper sulfate is treated with a similar solution of 50 g. of crystallized sodium sulfite. The greenish brown precipitate is collected, washed with water (Note 2), and then stirred into a solution of 100 g. (1.45 moles) of sodium nitrite in 400 ml. of water contained in a 2-l. beaker provided with an efficient mechanical stirrer.

The cold aqueous solution of the diazonium salt is then added slowly to the decomposition mixture. Considerable frothing occurs, and 4–5 ml. of ether is added from time to time to break the foam. After stirring for 1 hour (Note 3), the mixture is filtered and the crude dark brown precipitate of the 1,4-dinitronaphthalene is washed several times with water, then with 2% aqueous sodium hydroxide, and again with water. The precipitate is dried and extracted three times with boiling 95% ethanol (450 ml. in all). The extract is concentrated to 75 ml.; most of the 1,4-dinitronaphthalene separates and is collected. Additional amounts can be obtained by further concentration. The resulting product melts at 130–132° and weighs 6.0–7.0 g. (52–60%). The product can be purified either by steam distillation (Note 4) or by recrystallization from aqueous ethanol. Pale yellow needles melting at 134° are obtained (Notes 5 and 6).

2. Notes

1. This precipitate is sometimes sticky. It can be made granular by treating it with a small amount of 95% ethanol (after the removal of the supernatant liquid). Alternately, it may suffice to keep the ethereal diazotized solution cold and scratch the sides of the beaker with a glass rod.

2. The cupro-cupri sulfite of this variety is more efficient as a decomposition reagent than the red-violet precipitate obtained by treating a hot solution of copper sulfate with a solution of ammonium sulfite saturated with sulfur dioxide and subsequently heating the mixture for 10 minutes at 90°.

3. The decomposition appears to be immediate, and at the end of 1 hour most of the inorganic material has passed into solution.

4. Steam distillation of 1,4-dinitronaphthalene is very slow. However, the cupro-cupri sulfite method ¹ is a general one for the replacement of the diazonium group by the nitro group, and steam distillation is preferable whenever the product is readily volatile.

5. The solution is decolorized with charcoal in the course of the recrystallization. The checkers obtained 5 g. (43%) of golden needles after three recrystallizations.

6. 1,2-Dinitronaphthalene may be obtained similarly from 2-nitro-1-naphthylamine, or less satisfactorily from 1-nitro-2-naphthylamine; 1,6- and 2,6-dinitronaphthalenes can be prepared from the 5-nitro- and 6-nitro-2-naphthylamines, respectively, by a modification of the process. Since the solubility of these amines in glacial acetic acid is slight, it is preferable to prepare the diazonium sulfate as follows: Ten grams of the amine is dissolved in 50 ml. of sulfuric acid (sp. gr. 1.84), and the solution is mixed with one of 10 g. of sodium nitrite in 50 ml. of sulfuric acid (sp. gr. 1.84). This mixture is stirred into 200 ml. of glacial acetic acid. The temperature is maintained below 20° throughout these operations. After 30 minutes, the diazonium sulfate is precipitated at 0° by the addition of 200–500 ml. of ether as previously described.

3. Methods of Preparation

1,4-Dinitronaphthalene has been prepared previously from diazotized 4-nitro-1-naphthylamine by a modified Sandmeyer procedure,^{2,3} from 5,8-dinitrotetralin by dehydrogenation,⁴ by the deamination of 1,4-dinitro-2-naphthylamine,⁵ and by the decomposition of 4-nitro-1-naphthalenediazonium cobaltinitrite.⁶ The method described above has been published.¹

¹ Hodgson, Mahadevan, and Ward, *J. Chem. Soc.*, **1947**, 1392.

² Vesely and Dvorak, *Bull. soc. chim. France*, **33**, 319 (1923).

³ Contardi and Mor, *Rend. ist. lombardo sci.*, **57**, 646 (1924) [*C.A.*, **19**, 827 (1925)].

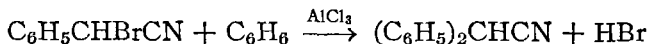
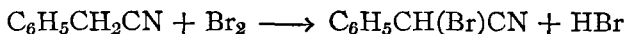
⁴ Chudozilov, *Collection Czechoslov. Chem. Commun.*, **1**, 302 (1929) [*C.A.*, **23**, 4212 (1929)].

⁵ Hodgson and Hathway, *J. Chem. Soc.*, **1945**, 453.

⁶ Hodgson and Ward, *J. Chem. Soc.*, **1947**, 127.

DIPHENYLACETONITRILE

(Acetonitrile, diphenyl-)



Submitted by C. M. ROBB and E. M. SCHULTZ.

Checked by RICHARD T. ARNOLD and J. W. BRITAIN.

1. Procedure

A. *α -Bromo- α -phenylacetonitrile.* In a well-ventilated hood (Note 1), a dry 500-ml. round-bottomed three-necked flask is equipped with a sealed stirrer, an air condenser (Note 2), and a cork carrying a dropping funnel and a thermometer. In the flask is placed 117 g. (1 mole) of benzyl cyanide (Note 3). The thermometer is adjusted so that the bulb is immersed in the benzyl cyanide. The flask is placed in a bath and heated to 105–110° (inside temperature). With good stirring, 176 g. (1.1 moles) of bromine (Note 4) is added over a period of 1 hour; during the addition and for 15 minutes thereafter the temperature of the liquid is maintained at 105–110°. At the end of the heating period the evolution of hydrogen bromide gas has practically ceased. The dropping funnel is replaced by a cork carrying a glass tube reaching to within 2–3 cm. of the surface of the reaction mixture. Dry nitrogen is then led through the apparatus for 30 minutes. The hot mixture is poured into the 500-ml. addition funnel fitted to the apparatus to be used in the next step (see part B). The reaction flask is rinsed with 100 g. (1.3 moles) of dry benzene (Note 5), and this is added to the bromonitrile. The benzene solution thus obtained is used immediately in the next step (Note 6).

B. *Diphenylacetonitrile.* A dry 2-l. round-bottomed three-necked flask, equipped with a sealed stirrer, a 500-ml. dropping funnel, and a dry reflux condenser (Note 2), is mounted on a

steam bath. In the flask are placed 368 g. (4.7 moles) of dry benzene (Note 5) and 133.5 g. (1 mole) of powdered anhydrous aluminum chloride. The stirrer is started, and the benzene is heated to vigorous refluxing. The α -bromo- α -phenylacetonitrile solution is added to the boiling mixture over a period of 2 hours in small portions (Note 7). After the addition is complete, the reaction mixture is refluxed for an additional hour. The flask is cooled, and the mixture is poured into a stirred mixture of 1 kg. of crushed ice and 100 ml. of concentrated hydrochloric acid in a 3-l. beaker.

The benzene layer is separated. The aqueous layer is extracted with 500 ml. of ether in two equal portions. The ether and benzene solutions are combined and washed successively with 500 ml. of water, 250 ml. of saturated sodium bicarbonate solution, and 500 ml. of water. The organic layer is dried over 100 g. of anhydrous sodium sulfate. The drying agent is separated from the solution, and the solvents are removed by heating on a steam bath. The last traces of benzene are removed by vacuum distillation from a 250-ml. Claisen flask heated on a steam bath. The residue weighs about 190 g. A receiver is connected directly to the side arm (Note 8) of the Claisen flask, and the product is distilled under reduced pressure. It boils at $122\text{--}125^{\circ}/1\text{--}2$ mm. and crystallizes to a yellow solid which melts at $68\text{--}70^{\circ}$. The solid is recrystallized from isopropyl alcohol (1 ml. per g.); the flask containing the filtered hot solution is placed on an asbestos mat, and the solution is allowed to cool only to room temperature without shaking or stirring. The crystals are then collected and washed on the funnel with chilled isopropyl alcohol (one-fifth the volume used in the recrystallization). The product is dried in a vacuum desiccator over concentrated sulfuric acid or phosphorus pentoxide. The yield of pure white product, melting at $74\text{--}75^{\circ}$, is 97–116 g. (50–60% based on benzyl cyanide) (Note 9).

2. Notes

1. α -Bromo- α -phenylacetonitrile is a lachrymator.
2. The mouth of the condenser is fitted with a cork carrying

a short U-tube, to prevent condensed moisture from running back into the flask.

3. The benzyl cyanide used was a redistilled grade obtained from the Benzol Products Company.

4. Reagent grade bromine was used.

5. Reagent grade benzene was subjected to distillation until no droplets of water formed in the distillate. The residual benzene was used directly without further distillation or drying.

6. The checkers found that the work could be interrupted for as much as 1 day after the preparation of α -bromo- α -phenylacetonitrile without appreciable effect on the yield.

7. The reaction is vigorous, but it can be readily controlled by adding the bromonitrile frequently in small portions.

8. The flask must be of such a type that the side arm can be heated to prevent plugging by the solidified distillate.

9. A second crop, amounting to 10–15 g. and melting at 68–70°, can be obtained by chilling the mother liquor, but recrystallization of this fraction from isopropyl alcohol does not raise the melting point.

3. Methods of Preparation

Diphenylacetonitrile has been prepared by the dehydration of diphenylacetamide,¹⁻⁷ by the reaction of diphenylbromomethane and mercuric cyanide,⁸ by the reaction of diphenylacetic acid and lead thiocyanate,⁹ and by the removal of ammonia from diphenylacetamidine.¹⁰ The present method is a modification of that of Hoch.¹¹

¹ Neure, *Ann.*, **250**, 142 (1889).

² Zinsser, *Ber.*, **24**, 3556 (1891).

³ Norris and Klemka, *J. Am. Chem. Soc.*, **62**, 1432 (1940).

⁴ Rupe and Gisiger, *Helv. Chim. Acta*, **8**, 338 (1925).

⁵ Trivedi, Phalnikar, and Nargund, *J. Univ. Bombay*, **10**, 135 (1942) [*C.A.*, **37**, 622 (1943)].

⁶ Hellerman, Cohn, and Hoen, *J. Am. Chem. Soc.*, **50**, 1716 (1928).

⁷ Smith, *Ber.*, **71**, 634 (1938).

⁸ Anschutz, *Ann.*, **233**, 345 (1886).

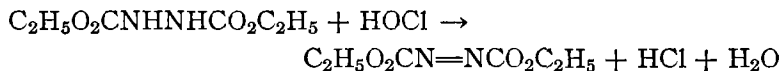
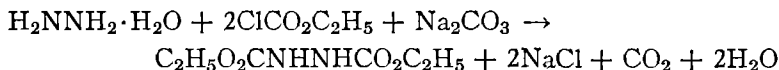
⁹ Wittig and Hopf, *Ber.*, **65**, 760 (1932).

¹⁰ Lipp, *Ann.*, **449**, 15 (1926).

¹¹ Hoch, *Compt. rend.*, **197**, 770 (1933).

ETHYL AZODICARBOXYLATE

(Formic acid, azobis-, diethyl ester)



Submitted by NORMAN RABJOHN.

Checked by H. J. SAMPSON and R. S. SCHREIBER.

1. Procedure

A. Ethyl hydrazodicarboxylate. In a 2-l. three-necked flask, equipped with a mechanical stirrer, two 500-ml. dropping funnels, and a thermometer (Note 1), is placed a solution of 59 g. (1 mole) of 85% hydrazine hydrate in 500 ml. of 95% ethanol. The reaction flask is cooled by means of an ice bath. When the temperature of the solution has dropped to 10°, 217 g. (2 moles) of ethyl chloroformate is added dropwise with stirring at a rate sufficient to maintain the temperature between 15° and 20°. After one-half of the ethyl chloroformate has been introduced, a solution of 106 g. (1 mole) of sodium carbonate in 500 ml. of water is added dropwise simultaneously with the remaining ethyl chloroformate. The addition of these two reactants is regulated so that the temperature does not rise above 20° and so that the addition of the chloroformate is completed slightly in advance of the sodium carbonate in order to ensure a slight excess of ethyl chloroformate in the reaction mixture at all times.

After all the reactants have been added, the precipitate on the upper walls of the flask is washed down with 200 ml. of water and the reaction mixture is allowed to stir for an additional 30-minute period. The precipitate is then collected on a Büchner funnel, washed well with a total of 800 ml. of water, and dried in an oven at 80°. There is obtained 145–150 g. (82–85%) of ethyl

hydrazodicarboxylate which melts at 131–133°. It is sufficiently pure (Note 2) for the preparation of ethyl azodicarboxylate.

B. *Ethyl azodicarboxylate*. A mixture of 100 g. (0.57 mole) of ethyl hydrazodicarboxylate, 500 ml. of benzene, and 500 ml. of water is placed in 2-l. three-necked flask equipped with a mechanical stirrer and a gas inlet tube. The flask and contents are tared, the flask is placed in an ice bath, and a slow stream of chlorine is bubbled into the mixture with stirring. The temperature is maintained below 15°, and chlorine is introduced until the increase in weight amounts to 50–55 g. (Note 3). The flow of chlorine is stopped and the reaction mixture is stirred until a clear, orange-colored benzene layer forms when the mixture is allowed to settle.

The layers are separated, and the water layer is extracted once with benzene. The benzene solutions are combined and washed twice with 100-ml. portions of water, then with 100-ml. portions of 10% sodium bicarbonate solution until neutral (usually four to six washes are required), twice more with water, and then are dried over anhydrous sodium sulfate. The benzene is removed under reduced pressure on a steam bath, and the residue is distilled in vacuum through a short indented column. After a small fore-run, the main fraction is collected at 107–111°/15 mm. There is obtained 80–82 g. (81–83%) of ethyl azodicarboxylate.

2. Notes

1. The thermometer and one of the funnels are fitted to a two-necked adapter; the thermometer scale must be such that the range between 10° and 20° is easily visible, preferably outside the flask, when the bulb is inserted in the liquid.

2. Ethyl hydrazodicarboxylate may be purified by crystallization from dilute ethanol; m.p. 134–135°.

3. A larger excess of chlorine causes the formation of higher-boiling materials and lowers the yield of ethyl azodicarboxylate.

3. Methods of Preparation

Ethyl hydrazodicarboxylate can be prepared by the reaction of ethyl chloroformate with hydrazine hydrate¹ or hydrazine sulfate in the presence of potassium hydroxide.² It can be prepared also by the treatment of symmetrical hydrazinedicarboxylic acid diazide with ethyl alcohol.³

Ethyl azodicarboxylate can be prepared by treating ethyl hydrazodicarboxylate with concentrated nitric acid² or a mixture of concentrated and fuming nitric acid.^{4, 5}

¹ Curtius and Heidenreich, *J. prakt. Chem.*, **52**, 476 (1895).

² Ingold and Weaver, *J. Chem. Soc.*, **127**, 381 (1925).

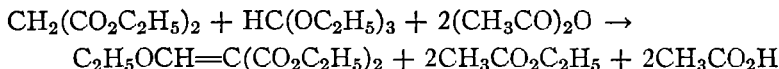
³ Stolle, *Ber.*, **43**, 2470 (1910).

⁴ Curtius and Heidenreich, *Ber.*, **27**, 774 (1894).

⁵ Diels and Fritzsche, *Ber.*, **44**, 3018 (1911).

ETHYL ETHOXYMETHYLENEMALONATE

(Malonic acid, ethoxymethylene-, diethyl ester)



Submitted by W. E. PARHAM and L. J. REED.¹

Checked by J. R. ROLAND, C. W. TODD, and R. S. SCHREIBER.

1. Procedure

A mixture of 1000 g. (6.75 moles) of ethyl orthoformate, 1260 g. (12.3 moles) of acetic anhydride, 960 g. (6.0 moles) of ethyl malonate, and 0.5 g. of anhydrous zinc chloride is prepared in a 5-l. three-necked flask equipped with a thermometer, a gas inlet tube, and a 12-in. column packed with Berl Saddles (Note 1). The column is attached to a still head and condenser. The contents of the flask are well agitated for 5 minutes by a stream of dry air and then heated (Note 2) as follows: 102–115° for 2½ hours, 115–127° for 7 hours [after the eighth hour of heating, 250

g. (2.45 moles) of acetic anhydride and 200 g. (1.35 moles) of ethyl orthoformate are added], 127–145° for 2 hours, and 145–155° for 2 hours (Note 3). At the end of 13½ hours of heating the mixture is cooled to room temperature and filtered (Note 4). The filtrate is distilled under reduced pressure (15–20 mm.) until the temperature at the still head reaches 100° (Note 5). The distillation is then continued under lower pressure (0.25 mm.). The yield of ethyl ethoxymethylenemalonate, b.p. 108–110°/0.25 mm. (Note 6), is 650–780 g. (50–60% based on the ethyl malonate used).

2. Notes

1. The use of this column prevents loss of acetic anhydride during the heating process and permits volatile products formed during the reaction to be removed by distillation. The checkers used a 1 by 12 in. column packed with 6 by 6 mm. glass rings.

2. The zinc chloride dissolves, and a chlorine-free crystalline precipitate soon separates. The checkers observed only traces of this precipitate.

3. The final heating is necessary to convert unchanged ethyl diethoxymethylmalonate, an intermediate in the reaction, into ethyl ethoxymethylenemalonate. This intermediate is difficult to separate from ethyl ethoxymethylenemalonate by distillation, and it is important that it be converted as completely as possible during the heating process.

4. The mixture is filtered through a fluted filter paper to remove suspended zinc salts.

5. Unchanged ethyl malonate (as much as 15% of the amount used) can be obtained by redistillation of the fraction boiling at 70–100°/17 mm.

6. Since ethyl diethoxymethylmalonate is difficult to separate from ethyl ethoxymethylenemalonate by distillation, it is necessary to follow the course of the distillation by observation of the change in refractive index instead of the change in boiling point. After a low-boiling fraction is collected, there is obtained an intermediate fraction (n_D^{20} 1.4142–1.4580), the size of which depends upon the amount of ethyl diethoxymethylmalonate present.

Under the best of conditions it amounts to 15 g. In each of three runs, the checkers obtained about 300–400 g. of material having a refractive index in this range.

The ethyl ethoxymethylenemalonate was collected at n_D^{20} 1.4580–1.4623. The checkers used a 5-in. Vigreux column and observed that at the low pressures the boiling point of the distillate in several runs was about 10° lower than that reported by the submitters. For example, in one run at 0.25 mm. (gauge pressure) the boiling point of the distillate never rose above 97.2° ; however, the refractive indices of twelve 50-ml. fractions taken in the course of this distillation were all in the proper range, n_D^{20} 1.4612–1.4623.

Interruption of the heating during the reaction period should be avoided. In an experiment in which the heating was discontinued after about eight hours and resumed the next day the yield was about 50%.

3. Methods of Preparation

Ethyl ethoxymethylenemalonate has been prepared by heating ethyl orthoformate, ethyl malonate, and acetic anhydride in the presence of zinc chloride.^{2,3} A higher yield of purer product is obtained by the method described above,⁴ which is a modification of the Claisen procedure.

¹ Work done under contract with the Office of Scientific Research and Development.

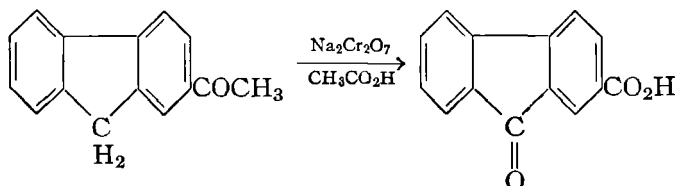
² Claisen, *Ber.*, **26**, 2729 (1893); *Ann.*, **297**, 76 (1897).

³ Wheeler and Johns, *Am. Chem. J.*, **40**, 237 (1908).

⁴ Fuson, Parham, and Reed, *J. Org. Chem.*, **11**, 194 (1946).

FLUORENONE-2-CARBOXYLIC ACID

(2-Fluorenenecarboxylic acid, 9-oxo-)



Submitted by GEORGE RIEVESCHL, Jr., and F. E. RAY.

Checked by R. L. SHRINER and ARNE LANGSJOEN.

1. Procedure

A 5-l. three-necked round-bottomed flask (Note 1) equipped with a mercury-sealed stirrer, a reflux condenser, and a dropping funnel is set up on a steam bath. In the flask are placed 50 g. (0.24 mole) of 2-acetylfluorene (p. 3) (Note 2) and 650 ml. of glacial acetic acid. After the ketone has been brought into solution by heating and stirring, 450 g. (1.5 moles) of sodium dichromate dihydrate, previously ground to a coarse powder, is added carefully in small portions (about 10 g. each) (Note 3). Heating and stirring are continued throughout the addition, which requires about 45 minutes. The reaction flask is then removed from the steam bath, and the solution is brought to gentle reflux over a flame. During a period of 90 minutes, 200 ml. of acetic anhydride is added through the dropping funnel. The mixture is refluxed and stirred during this addition and for 8 hours longer (Note 4).

The hot mixture is stirred into 9 l. of hot water in a 5-gal. crock. The suspension is agitated for 15 minutes and is then filtered on a 24-cm. Büchner funnel. The filter cake is washed with four 400-ml. portions of 2% sulfuric acid. The wet filter cake is transferred to a 2-l. beaker containing 700 ml. of a 5% solution of potassium hydroxide (Note 5). The mixture is stirred

and heated to about 80°, and the hot solution is filtered. The alkali-insoluble material (Note 6) is washed with 50 ml. of hot 5% potassium hydroxide solution, and the combined alkaline filtrates are placed in a beaker, stirred with 5 g. of decolorizing carbon for 20 minutes, and again filtered. The solution of the potassium salt is heated with vigorous mechanical stirring to 70°, and 200 ml. of 18% hydrochloric acid is added dropwise, the heating being continued so that the temperature rises to about 85°. The fluorenone-2-carboxylic acid separates as a thick yellow mass. It is allowed to digest for 10 minutes with stirring, and the hot mixture is filtered on a 24-cm. Büchner funnel. The acid is washed free of potassium chloride by five or six 200-ml. portions of hot water. The product is pressed as dry as possible and then dried for 3 hours in an oven at 150°. It is a bright canary-yellow, weighs 36–40 g. (67–74%), and melts on an aluminum block at 339–341° (uncor.) with partial sublimation (Note 7).

2. Notes

1. A relatively large flask is used so that the sodium dichromate may be added without the escape of much acetic acid vapor.

2. 2-Acetylfluorene melting at 124–126° has been found to give as good results as the pure compound of melting point 128–129°. The submitters report that the over-all yield from fluorene to fluorenone-2-carboxylic acid can be improved by the use of the crude product of the acylation (m.p. 113–117°) without purification (p. 4).

3. The acetic acid solution of 2-acetylfluorene is conveniently and safely heated to the maximum temperature attainable on the steam bath, and then small portions of sodium dichromate are added as the speed of the reaction permits. To prevent a violent reaction, not more than 10 g. of dichromate is added until the oxidation has begun (as indicated by the appearance of a green color).

4. Small yellow crystals usually appear after the mixture has refluxed for about 7 hours; their quantity does not increase much during the remaining heating period.

5. Sodium hydroxide should not be substituted here because of the lower solubility of the sodium salt.

6. The alkali-insoluble material (3–9 g.) can be washed with water, dried, and recrystallized from 95% ethanol to yield from 1 to 5 g. of pure 2-acetylfluorenone melting at 154–155°. Alternatively, it can be added to the next lot of 2-acetylfluorene if another oxidation is to be carried out.

7. This melting point corresponds to that given in the literature.^{1,2} The submitters report that the product can be recrystallized from acetic anhydride or Cellosolve.

3. Methods of Preparation

The method described is a modification of the method of Dziejowski and Schnayder¹ and is described in a patent by the submitters.² Fluorenone-2-carboxylic acid has also been obtained by the oxidation of 2-fluorenealdehyde.³

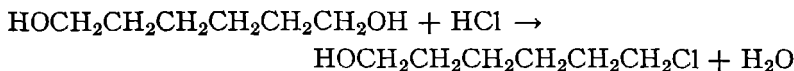
¹ Dziejowski and Schnayder, *Bull. intern. acad. polon. sci.*, **1930A**, 529 [*C.A.*, **25**, 5416 (1931)].

² Rieveschl and Ray, U. S. pat. 2,377,040 [*C.A.*, **39**, 3305 (1945)].

³ Hinkel, Ayling, and Beynon, *J. Chem. Soc.*, **1936**, 345.

HEXAMETHYLENE CHLOROHYDRIN

(1-Hexanol, 6-chloro-)



Submitted by KENNETH N. CAMPBELL and ARMIGER H. SOMMERS.¹

Checked by RICHARD T. ARNOLD and ROGER AMIDON.

1. Procedure

The apparatus shown in Fig. 1 is constructed from a 1-l. distilling flask (*A*) and a 500-ml. distilling flask (*B*) the side arm of which has been replaced by 10-mm. Pyrex tubing sealed at an

upward angle to the side arm of the larger flask (*A*). Charred cork stoppers are used, and a hydrogen chloride trap² is connected to the water-cooled reflux condenser. The bent side arm (*C*) is insulated by a wrapping of cloth. Reaction flask *A* is charged with 105 g. (0.89 mole) of hexamethylene glycol,³ 785 ml. (9.5 moles) of concentrated hydrochloric acid, 130 ml. of water (Note 1), and 55 ml. of toluene (Notes 2 and 3). In flask *B* are put 350

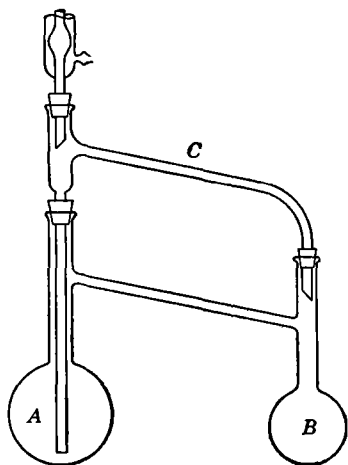


FIG. 1

ml. of toluene and a few boiling chips. The apparatus is assembled, and the flasks are heated in oil baths. The bath covering about two-thirds of flask *A* is kept at 95°; the one surrounding most of flask *B* is kept between 160° and 165° (Note 4). As the reaction proceeds and the products are removed by the continuous flow of toluene through the mixture, the organic-aqueous interface in *A* falls steadily. After 9 hours the heating baths and condensers are removed, and water is added to *A* to force the

upper layer of toluene into *B*. The aqueous solution is siphoned out of *A*, and then the toluene extract in *B* is poured into a dropping funnel inserted through a stopper in the neck of a 500-ml. Claisen flask. Some of the extract is run into the flask, and most of the toluene is removed by distillation at atmospheric pressure while the remainder of the solution is slowly run into the flask. To remove the last of the solvent, the pressure is lowered to 65 mm. while the bath temperature is kept at 100°.

The material obtained from two such runs is combined and fractionated through a Fenske-Whitmore column⁴ packed with glass helices. Distillation is carried out at a pressure of 8–12 mm., with a reflux ratio of 5:1. After a fore-run of 5–15 g., about 45 g. (16%) of hexamethylene dichloride distils at 80–84°/9 mm., n_D^{20} 1.4585–1.4565. An intermediate fraction of 10–20 g. distils at

84–100°/9 mm., and then 108–122 g. (45–50%) of hexamethylene chlorohydrin boiling at 100–104°/9 mm., n_D^{20} 1.4551–1.4557, is collected. If several runs are made the residues may be distilled from a Claisen flask and the distillate combined with the intermediate fractions for refractionation. In this way the average yield may be raised to 50–55%.

2. Notes

1. The use of concentrated hydrochloric acid without dilution results in violent bubbling during the reaction.

2. In the original work of Bennett and Turner⁵ a petroleum fraction of b.p. 90–120° was used. When the submitters used Skellysolve L, b.p. 90–100°, the hexamethylene chlorohydrin was not sufficiently soluble in it to be removed from the reaction mixture. A study of the solubility of hexamethylene chlorohydrin in various commonly available solvents was made, and toluene was found to be the most satisfactory.

3. The exact volume of free space below the side arm of *A* will vary somewhat according to the exact dimensions of the flask and the adapter tube, and it may be desirable to make corresponding changes in the volumes of hydrochloric acid and water used. In the apparatus constructed by the checkers the aqueous phase expanded during the heating to such an extent that only about 5 ml. of toluene remained in the neck below the side arm; this apparatus operated satisfactorily when the volumes of hydrochloric acid and water were reduced to 720 ml. and 115 ml., respectively.

4. The bath temperature may be controlled by heating with an immersed loop of Nichrome resistance coil, such as the heating element from an electrical appliance. The coil is connected to a 110-volt line in series with a 27-ohm 5-ampere variable resistor and a 600-watt heater element, which may be cut out of the circuit to lower the fixed resistance. An ammeter in the circuit helps to determine the proper adjustment of the sliding contact of the resistor. To avoid an excessive load on the coil,

the bath about *B* should be heated in addition by a hot plate adjusted to give a temperature somewhat below 160°.

3. Methods of Preparation

Hexamethylene chlorohydrin has been prepared by the reaction of hydrochloric acid with hexamethylene glycol, without a catalyst ⁵ or in the presence of cuprous chloride.⁶

¹ Work done under contract with the Office of Scientific Research and Development.

² *Org. Syntheses* Coll. Vol. 2, 4 (1943).

³ *Org. Syntheses* Coll. Vol. 2, 325 (1943).

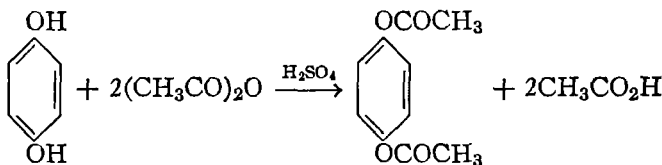
⁴ *Org. Syntheses*, 25, 2 (1945).

⁵ Bennett and Turner, *J. Chem. Soc.*, 1938, 814.

⁶ Coleman and Bywater, *J. Am. Chem. Soc.*, 66, 1821 (1944).

HYDROQUINONE DIACETATE

(Quinol, diacetate)



Submitted by W. W. PRICHARD.

Checked by HOMER ADKINS and MAYNETTE VERNSTEN.

1. Procedure

One drop of concentrated sulfuric acid is added to a mixture of 110 g. (1.0 mole) of hydroquinone and 206 g. (190.3 ml., 2.02 moles) of acetic anhydride (Note 1) in a 1-l. Erlenmeyer flask. The mixture is stirred gently by hand; it warms up very rapidly, and the hydroquinone dissolves. After 5 minutes the clear solution is poured onto about 800 ml. of crushed ice. The white crystalline solid which separates is collected on a Büchner filter and washed with 1 l. of water. The filter cake is pressed occa-

sionally to facilitate the removal of water; the solid is dried to constant weight over phosphorus pentoxide in a vacuum desiccator. The nearly pure product weighs 186–190 g. (96–98%) and melts at 121–122° (Note 2); it can be recrystallized from dilute ethanol (Note 3).

2. Notes

1. The use of commercial acetic anhydride in this preparation sometimes results in appreciably lower yields. The checkers used the freshly redistilled reagent.

2. The melting point is recorded in the literature ^{1,2} as 121° and as 123–124°.

3. Recrystallization from 50% ethanol (by weight) permits a 93–94% recovery of material melting at 121.5–122.5°; about 365 g. (400 ml.) of the solvent is required for 100 g. of the crude product.

3. Methods of Preparation

Hydroquinone diacetate has been prepared by the treatment of hydroquinone with acetic anhydride, both in the presence ^{1,3,4} and in the absence ^{5,6,7} of strong acid catalysts, by the treatment of the sodium salt of hydroquinone with acetic anhydride, and by the reaction of hydroquinone with acetic anhydride in the presence of sodium acetate.^{8,9} It has also been prepared from hydroquinone and acetyl chloride;¹⁰ the acetylation with acetyl chloride is reported to be improved by the addition of metallic magnesium.¹¹

¹ Ciusa and Sollazzo, *Chem. Zentr.*, **114**, II, 615 (1943).

² Chattaway, *J. Chem. Soc.*, **1931**, 2495.

³ Henle, *Ann.*, **350**, 344 (1906).

⁴ Reychler, *Chem. Zentr.*, **79**, I, 1042 (1908).

⁵ Shaw, *J. Chem. Soc.*, **99**, 1610 (1911).

⁶ Hesse, *Ann.*, **200**, 244 (1880).

⁷ Kaufmann, *Ber.*, **42**, 3482 (1909).

⁸ Sarauw, *Ann.*, **209**, 128 (1881).

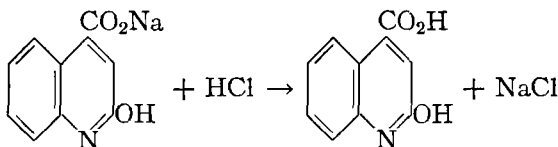
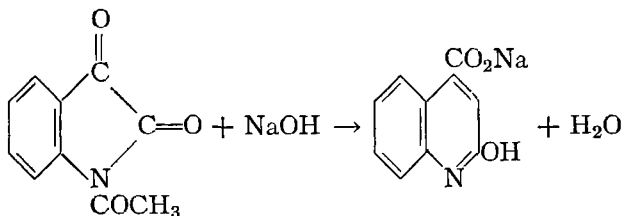
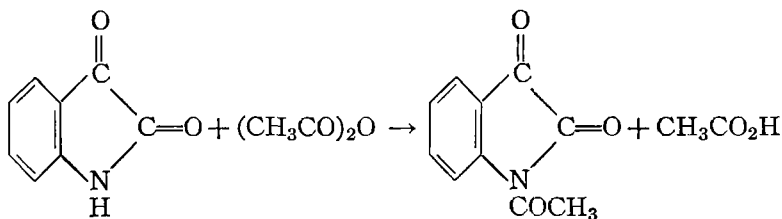
⁹ Buchka, *Ber.*, **14**, 1327 (1881).

¹⁰ Nietzki, *Ber.*, **11**, 470 (1878).

¹¹ Spasov, *Ann. univ. Sofia II, Faculté phys.-math.*, livre 2, **35**, 289 (1938–1939) [*C.A.*, **34**, 2343 (1940)].

2-HYDROXYCINCHONINIC ACID

(Cinchoninic acid, 2-hydroxy-)



Submitted by THOMAS L. JACOBS, S. WINSTEIN, GUSTAVE B. LINDEN,
 JEAN H. ROBSON, EDWARD F. LEVY, and DEXTER SEYMOUR.¹
 Checked by R. T. ARNOLD and F. M. ROBINSON.

1. Procedure

A. *N-Acetylisatin*. In a 3-l. three-necked flask equipped with a mercury-sealed stirrer and reflux condenser are placed 600 g. (4.1 moles) of isatin (Note 1) and 1390 ml. (14.7 moles) of acetic anhydride (Note 2). This mixture is refluxed for 4 hours over a free flame with constant stirring. The solution is allowed to cool slowly to room temperature with stirring and is then cooled to about 10° (Note 3). The slurry of crystals is collected on a 12-in.

Büchner funnel and washed with five 175-ml. portions of ether or until the washings are light red. The yield of crude air-dried N-acetylising, m.p. 141–142° (cor.), is 635 to 643 g. (82–83%) (Note 4).

B. *2-Hydroxycinchoninic acid*. To a solution of 160 g. (about 3.8 moles) of U.S.P. sodium hydroxide in 9.6 l. of water in a 12-l. flask is added 310 g. (1.64 moles) of crude N-acetylising. The mixture is stirred mechanically and heated to boiling; the flame is adjusted to maintain gentle boiling. After the mixture has boiled 1 hour (Note 5) the flame is removed, 50 g. of decolorizing carbon is added cautiously (vigorous boiling and frothing may occur if the solution is too hot), and the suspension is stirred for 30 minutes. The charcoal is allowed to settle for a few minutes, and the solution is siphoned into a filter funnel containing a layer of Supercel. The filtrate is allowed to cool overnight in a 5-gal. crock. The solution is stirred with a hook-type stirrer driven by a powerful motor (Note 6), and 6 N hydrochloric acid is added until the mixture is neutral to Congo red. The suspension is filtered immediately (Note 7) through a 12-in. Büchner funnel, and the solid is washed with 2 l. of water. The filtrate is made distinctly acid to Congo red and set aside for a few hours. The solid acid is dried at 90° for 2 days; the anhydrous acid, m.p. 346–347° (cor.), so obtained has the correct neutral equivalent (Note 8) and weighs 200 to 205 g. (70–73% over-all yield, based on isatin consumed). From the acidified filtrate, after precipitation is complete, about 60 g. of isatin is recovered.

2. Notes

1. Commercial isatin, m.p. 199.0–200.5° (cor.), was obtained from the National Aniline and Chemical Company.

2. Acetic anhydride obtained from the Carbide and Carbon Chemicals Corporation was employed. Redistillation of this reagent did not increase the yield.

3. If the solution is not stirred during the cooling, the product crystallizes as a solid cake which is difficult to remove from the flask.

4. Recrystallization from benzene, unnecessary for the present purpose, gives a yellow crystalline product of m.p. 142.0–143.5° (cor.).

5. It is convenient to make two of these runs simultaneously. A reflux condenser is unnecessary, but if none is used the stopper holding the stirrer must be provided with a vent to permit steam to escape.

6. The ordinary small laboratory stirring motor is insufficiently powerful to maintain rapid agitation after most of the cinchoninic acid has precipitated.

7. If the mixture is not filtered immediately after acidification, or if the first end point is overrun, isatin is precipitated along with the cinchoninic acid and the product has a deep red color. Such material can be freed of isatin by dissolving it in sodium bicarbonate solution, filtering, and reprecipitating.

8. This crude acid, which is satisfactory for most purposes, can be recrystallized from glacial acetic acid to yield a product melting at 352–353° (cor.).

3. Methods of Preparation

2-Hydroxycinchoninic acid has been prepared by the rearrangement of N-acetylisatin in alkali,^{2,3,4} by the treatment of isatin with malonic acid in glacial acetic acid,⁵ and by heating cinchoninic acid with concentrated potassium hydroxide.⁶

¹ Work done under contract with the Office of Scientific Research and Development.

² Camps, *Arch. Pharm.*, **237**, 659 (1899).

³ Ainley and King, *Proc. Roy. Soc. London*, **125B**, 60 (1938).

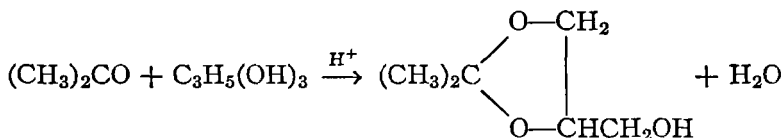
⁴ Campbell and Kerwin, *J. Am. Chem. Soc.*, **68**, 1837 (1946).

⁵ Borsche and Jacobs, *Ber.*, **47**, 354 (1914).

⁶ Koenigs and Koerner, *Ber.*, **16**, 2152 (1883).

***dl*-ISOPROPYLIDENEGLYCEROL**

(Glycerol, isopropylidene-; also 1,3-dioxolane-4-methanol,
2,2-dimethyl-)



Submitted by MARY RENOLL and MELVIN S. NEWMAN.
Checked by R. L. SHRINER and ARNE LANGSJOEN.

1. Procedure

In a 1-l. three-necked flask, fitted with a sealed mechanical stirrer and a fractionating column (about 2 by 45 cm., packed with glass helices) attached to a total reflux phase-separating head (Fig. 2) (Note 1), are placed 237 g. (300 ml., 4.09 moles) of acetone (Note 2), 100 g. (1.09 moles) of glycerol (Note 3), 300 ml. of low-boiling petroleum ether (Note 4), and 3.0 g. of *p*-toluene-sulfonic acid monohydrate. The third neck is closed with a cork or a ground-glass stopper, and the mixture is heated (Note 5) with stirring so that the petroleum ether refluxes as rapidly as the column permits. The stirring and refluxing are continued until no more water collects in the trap of the separating head; the time required varies between 21 and 36 hours (Note 6).

The mixture is cooled to room temperature, and 3.0 g. of powdered, freshly fused sodium acetate is added. Stirring is continued for 30 minutes; the mixture is then filtered, and the petroleum ether and excess acetone are removed by distillation under reduced pressure (water pump). The residual liquid is distilled from a modified Claisen flask. The fraction boiling at 80–81°/11 mm. is collected. The yield of colorless isopropylideneglycerol (n_D^{25} 1.4339, d_4^{25} 1.062) is 125–129 g. (87–90%).

2. Notes

1. During operation, the apparatus shown in Fig. 2 requires no attention beyond occasional draining of the water trap. It is suitable for a number of preparations in which water is removed by distillation with an immiscible solvent; it functions only when the condensate separates into two phases, of which water is the more dense.

2. The acetone was the 99.5% grade obtained from the Carbide and Carbon Chemical Corporation.

3. The glycerol should be of U.S.P. grade; if it has absorbed moisture, it may be dehydrated by heating at 170° in an open dish under a hood for 3 hours.¹

4. Skellysolve F, b.p. 35–55°, obtainable from the Skelly Oil Company, is suitable.

5. The mixture may be heated by means of a steam or water bath, but in view of the long reflux period it is better to use a hemispherical electric heating mantle controlled by a variable transformer (Variac).

6. The period of refluxing need not be continuous. A longer reflux time, up to 70 hours, does not increase the yield. The volume of the aqueous phase collected in the separating head varies from 32 to 42 ml., depending on the quality of the glycerol.

3. Methods of Preparation

Isopropylideneglycerol has been prepared from acetone and glycerol in the presence of the following acidic catalysts: hydrogen chloride,^{2,3} hydrogen chloride and anhydrous sodium sulfate,⁴ phosphorus pentoxide,⁵ and anhydrous copper sulfate.⁶ It has also been prepared from acetone and glycerol in the presence of calcium carbide and

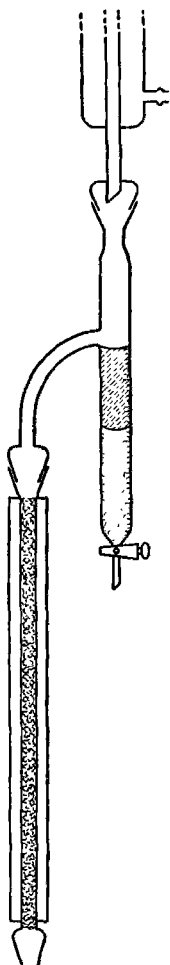


FIG. 2

a neutral surface-active agent.⁷ The two optically active isomers of isopropylideneglycerol have been prepared from 1,2,5,6-diacetone-D-mannitol and 1,2,5,6-diacetone-L-mannitol.⁸ The procedure given is based on the method of Newman and Renoll.⁹

¹ *Org. Syntheses* Coll. Vol. 1, 17 (1941).

² Fischer, *Ber.*, **28**, 1167 (1895).

³ Irvine, Macdonald, and Soutar, *J. Chem. Soc.*, **107**, 343 (1915).

⁴ Fischer and Pfähler, *Ber.*, **53**, 1607 (1920).

⁵ Smith and Lindberg, *Ber.*, **64**, 510 (1931).

⁶ Hibbert and Morazain, *Can. J. Research*, **2**, 38 (1930).

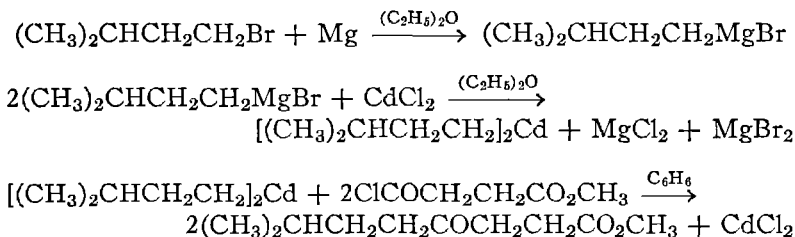
⁷ Maglio and Burger, *J. Am. Chem. Soc.*, **68**, 529 (1946).

⁸ Baer and Fischer, *J. Biol. Chem.*, **128**, 468 (1939); *J. Am. Chem. Soc.*, **67**, 2035 (1945).

⁹ Newman and Renoll, *J. Am. Chem. Soc.*, **67**, 1621 (1945).

METHYL 4-KETO-7-METHYLOCTANOATE

(Caprylic acid, ζ -methyl- γ -oxo-, methyl ester)



Submitted by JAMES CASON and FRANKLIN S. PROUT.

Checked by HOMER ADKINS and ROBERT TURNER.

1. Procedure

A 2-l. three-necked flask (Note 1) is fitted with a reflux condenser having a take-off attachment,¹ a mercury-sealed Hershberg stirrer² (Note 2), and a 500-ml. dropping funnel (Note 1). A nitrogen inlet tube is connected to the top of the condenser, and a branch of the tube, connected by means of a T-tube, is connected to a mercury valve¹ consisting of a U-tube, the bend of which is just filled with mercury. Unless the dropping funnel is

equipped with a pressure-equalizing side tube,¹ a second branch of the nitrogen line is arranged for connection to its mouth. In the flask is placed 24.3 g. (1.0 gram atom) of magnesium turnings, and the entire flask is warmed with a soft flame while a slow stream of nitrogen is passed through and permitted to escape by way of the dropping funnel. The flask is allowed to cool, the dropping funnel is closed, and the nitrogen flow is reduced until the gas bubbles very slowly through the mercury valve. The magnesium is covered with 150 ml. of dry ether, introduced from the dropping funnel, and a solution of 151 g. (1.0 mole) of pure isoamyl bromide (Note 3) in 350 ml. of dry ether is placed in the dropping funnel. A few milliliters of the bromide solution is added to the flask, and the stirrer is started. The flask is warmed gently if the reaction does not start spontaneously. The remainder of the bromide is added during 1 to 2 hours, and the mixture is refluxed for 15 minutes longer. The flask is then cooled in an ice bath, the dropping funnel is removed, and 98 g. (0.535 mole) of anhydrous c.p. cadmium chloride (Note 4) is added over a period of 5–10 minutes. After all the cadmium chloride has been added, the ice bath is removed and the mixture is stirred for 5 minutes and then heated under reflux with stirring for an additional 45 minutes (Note 5).

Ether is now rapidly distilled from the reaction mixture (Note 6) by heating on a steam bath. Distillation is continued with stirring until it becomes very slow and a dark viscous residue remains. The distillate amounts to 250–325 ml. At this point, 350 ml. of dry thiophene-free benzene is added to the flask and the distillation is continued until an additional 100 ml. of distillate has been collected. A second 350-ml. portion of dry benzene is added to the flask, and the mixture is refluxed with vigorous stirring for a few minutes in order to break up the cake in the flask and disperse it through the mixture. The heating bath is then removed, and 120 g. (0.8 mole) (Note 7) of β -carbomethoxypropionyl chloride ³ in 150 ml. of dry benzene is added from the dropping funnel. This addition, which causes vigorous refluxing, requires 10–20 minutes. During this time the heavy precipitate changes in appearance and stirring becomes more difficult. After

the addition of the acid chloride is complete and spontaneous refluxing has stopped, the mixture is stirred and heated under reflux for an additional hour.

The reaction mixture is cooled in an ice bath and decomposed in the usual way by the careful addition of about 600 g. of ice and water, followed by sufficient 20% sulfuric acid to give two clear phases (Note 2). The aqueous phase is separated in a 2-l. separatory funnel and extracted with two 100-ml. portions of benzene. The two benzene extracts are placed in two 500-ml. separatory funnels. The original benzene layer and each extract are washed successively (Note 8) with 200 ml. of water, 200 ml. of 5% sodium carbonate solution, 200 ml. of water, and 100 ml. of saturated sodium chloride solution, and then each is filtered through a layer of anhydrous sodium sulfate. A little fresh solvent is used to rinse the separatory funnels and the filter.

A fractionating column (Note 9) is connected to a 250-ml. flask carrying a dropping funnel and heated in an oil bath at 150–160°. The combined benzene solutions are run into the flask from the dropping funnel so that the benzene is removed by flash distillation at atmospheric pressure. The pressure is then lowered, and after the distillation of the last of the solvent and a little 2,7-dimethyloctane (from coupling of the Grignard reagent) the vapor temperature rises to about 100°/20 mm. About 5 g. of methyl ethyl succinate (Notes 10 and 11) is collected at 100–106°/20 mm., and after an intermediate fraction (about 3 g.) the keto ester is collected at 136–137°/20 mm. (Notes 11 and 12). The yield of methyl 4-keto-7-methyloctanoate is 108.5–111.5 g. (73–75%, based on β -carbomethoxypropionyl chloride) (Notes 13 and 14).

2. Notes

1. Connections may be made with rubber stoppers, but ground-glass joints are preferable.

2. The heavy sludges encountered in this preparation make a strong and efficient stirrer essential. A stirrer of the Hershberg type of tantalum wire is preferable, but new, unetched Nichrome is quite satisfactory. If a Nichrome stirrer is used it should be

removed before acid is added to complete the decomposition of the organometallic complex.

3. Isoamyl bromide, b.p. 120–120.5°, was prepared as previously described.⁴ The product was fractionated through a packed column, such as that referred to in Note 9 below, to remove small quantities of *tert.*-amyl bromide arising from *sec.*-butyl carbinol present in the isoamyl alcohol.

4. The cadmium chloride is dried to constant weight at 110° in an oven, ground thoroughly, and stored in a desiccator. If stored in a screw-cap bottle in the laboratory it may absorb moisture slowly.

5. It is best to continue stirring at this point until the mixture gives a negative Gilman test for the Grignard reagent.⁵ One-half milliliter of the reaction mixture is added to an equal volume of a 1% solution of Michler's ketone in dry benzene. After this mixture is shaken briefly, 1 ml. of water is added, followed by a few drops of a 0.2% solution of iodine in glacial acetic acid and 0.5 ml. of glacial acetic acid. If any Grignard reagent is still present, a greenish blue color is observed.

6. If the reaction with the acid chloride is carried out in ether solution larger amounts of methyl ethyl succinate are formed, and the yield of keto ester is only 42–59%.

7. The use of β -carbomethoxypropionyl chloride of poor quality frequently resulted in poor yields of the desired keto ester. It is most important that the methyl hydrogen succinate, m.p. 56–57°, from which the acyl chloride is prepared, be of high quality and that it be ground thoroughly before drying.³ The melting point of a sample of methyl hydrogen succinate is not a sufficient criterion of purity, so that the neutral equivalent of the sample of ester should be determined. If the neutral equivalent is not in the range 130–134, the reagent should be purified by recrystallization.

8. The indicated portion of each wash solution is used to wash each of the benzene solutions in turn. If three separatory funnels are used this process is not laborious and results in very thorough extraction.

9. An efficient column packed with glass helices and provided with a heating jacket and a suitable head ⁶ should be used. Columns of dimensions 50 cm. by 14 mm. i.d. and 43 cm. by 12 mm. i.d. have been found satisfactory.

10. The methyl ethyl succinate apparently results from the reaction of the acid chloride with ether.

11. The apparent boiling points of the fractions may vary somewhat, depending on the fractionating column.

12. Boiling points of the keto ester at other pressures are as follows: 117°/8 mm., 120–122°/11 mm., 125°/14 mm., 139.5°/22 mm., and 145°/27 mm.

13. In an alternative procedure the fractionating column is removed after the intermediate fraction has been collected, and the residual ester is distilled through a short still head.

14. The procedure described has been used by the submitters for the preparation of the following keto esters:

KETO ESTER	B.P.	% YIELD
Ethyl 10-keto-13-methyltetradecanoate	180–182°/3 mm.	85
Ethyl 10-keto-16-methyloctadecanoate	192–195°/2 mm.	76.5
Ethyl 6-ketoheptanoate	143–145°/33 mm.	76
Ethyl 10-ketohendecanoate	137–138°/2 mm.	83
Ethyl 10-keto-14-methyltetracosanoate	242–245°/1 mm.	77

The ester acid chlorides used in these preparations, ω -carbethoxyvaleryl chloride and ω -carbethoxynonanoyl chloride, were obtained from the corresponding half esters ⁷ in yields of 90–95%. The method described for β -naphthoyl chloride ⁸ was used, but since with these acids the reaction is much more vigorous the phosphorus pentachloride was added in small portions and the mixture was not heated until after the exothermic reaction had subsided.

The procedure described failed completely when a secondary bromide, 2-bromopentane, was used; however, when the cadmium derivative was prepared at -5° to -7° and allowed to react in ether at this temperature with β -carbomethoxypropionyl chloride, methyl 4-keto-5-methyloctanoate was obtained in a yield of 19.3%, b.p. 130.5–130.7°/21 mm.

3. Methods of Preparation

Methyl 4-keto-7-methyloctanoate has been prepared only by the procedure given, which is based on the method of Cason and Prout.⁹ The use of cadmium derivatives for the preparation of simple ketones was introduced by Gilman and Nelson.¹⁰

¹ Fieser, *Experiments in Organic Chemistry*, 2nd ed., p. 323, Fig. 49; p. 404, Fig. 75, D. C. Heath and Company, 1941.

² *Org. Syntheses* Coll. Vol. 2, 117 (1943).

³ *Org. Syntheses*, 25, 19 (1945).

⁴ *Org. Syntheses* Coll. Vol. 1, 27 (1941).

⁵ Gilman and Schulze, *J. Am. Chem. Soc.*, 47, 2002 (1925); Gilman and Heck, *J. Am. Chem. Soc.*, 52, 4949 (1930).

⁶ Whitmore and Lux, *J. Am. Chem. Soc.*, 54, 3448 (1932).

⁷ *Org. Syntheses* Coll. Vol. 2, 276 (1943).

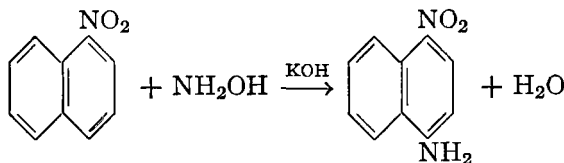
⁸ *Org. Syntheses*, 21, 86, Note 2 (1941).

⁹ Cason and Prout, *J. Am. Chem. Soc.*, 66, 46 (1944); Cason, *J. Am. Chem. Soc.*, 68, 2078 (1946); *Chem. Revs.*, 40, 15 (1947).

¹⁰ Gilman and Nelson, *Rec. trav. chim.*, 55, 518 (1936).

4-NITRO-1-NAPHTHYLAMINE

(1-Naphthylamine, 4-nitro-)



Submitted by CHARLES C. PRICE and SING-TUH VOONG.

Checked by RICHARD T. ARNOLD and JAY S. BUCKLEY, JR.

1. Procedure

Twenty grams (0.115 mole) of α -nitronaphthalene (Note 1) and 50 g. (0.72 mole) of powdered hydroxylamine hydrochloride are dissolved in 1.2 l. of 95% ethanol contained in a 3-l. flask which is heated in a bath maintained at 50–60°. A filtered solu-

tion of 100 g. of potassium hydroxide in 500 g. (630 ml.) of methanol is added gradually with vigorous mechanical stirring (Note 2) over a period of 1 hour. Stirring is continued for an additional hour, and the warm solution is poured slowly into 7 l. of ice water. After the solid has coagulated, it is collected on a filter and washed thoroughly with water. The crude 4-nitro-1-naphthylamine is purified by recrystallization from 500 ml. of 95% ethanol (Note 3). About 12–13 g. (55–60%) of long golden-orange needles, m.p. 190.5–191.5°, is obtained.

2. Notes

1. The α -nitronaphthalene, m.p. 56–57°, was obtained from Eastman Kodak Company.

2. The color changes from yellow to orange, and potassium chloride separates.

3. In some experiments a few milliliters of dilute hydrochloric acid (1:1) or sulfuric acid (1:1) was added to facilitate the crystallization of the 4-nitro-1-naphthylamine.

3. Methods of Preparation

This method is essentially that described by Goldhahn.¹ 4-Nitro-1-naphthylamine has also been prepared by the nitration of α -naphthylamine,² acetyl- α -naphthylamine,^{3,4} and ethyl-1-naphthyloxamate,^{5,6} by the oxidation of 4-nitroso-1-naphthylamine,⁷ and by reaction of 4-chloro-1-nitronaphthalene with ammonia.⁸

¹ Goldhahn, *J. prakt. Chem.*, **156**, 315 (1940); **157**, 96 (1940).

² Meldola and Streatfeild, *J. Chem. Soc.*, **63**, 1055 (1893).

³ Lellmann and Remy, *Ber.*, **19**, 796 (1886).

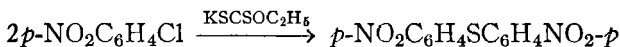
⁴ Hodgson and Walker, *J. Chem. Soc.*, **1933**, 1205.

⁵ Lange, Ger. pat. 58,227 [*Frdl.*, **3**, 509 (1890–1894)].

⁶ Sergievskaya, Russ. pat. 50,696 (1937); *J. Gen. Chem. U.S.S.R.*, **10**, 55 (1940).

⁷ Vorozhtsov and Kozlov, *J. Gen. Chem. U.S.S.R.*, **9**, 587 (1939).

⁸ Ger. pat. 117,006 [*Frdl.*, **6**, 176 (1900–1902)].

p*-NITROPHENYL SULFIDE*[Sulfide, *bis*-(*p*-nitrophenyl)]**

Submitted by CHARLES C. PRICE and GARDNER W. STACY.

Checked by CLIFF S. HAMILTON and PAUL D. BERRY.

1. Procedure

In a 1-l. round-bottomed flask equipped with a reflux condenser are placed 157.5 g. (1 mole) of *p*-chloronitrobenzene, 160 g. (1 mole) of potassium xanthate (Note 1), and 450 ml. of 95% ethanol. This reaction mixture is heated under reflux on a steam bath for 48 hours. The crystalline product, which deposits from solution during the course of the reaction, is collected by filtration, crushed into small particles in a mortar, and washed twice with hot ethanol and once with hot water. The yield of *p*-nitrophenyl sulfide melting at 158–160° is 105–113 g. (76–82%). This product is pure enough for most purposes. Recrystallization from glacial acetic acid (15 ml. per gram) raises the melting point to 160–161°.

2. Note

1. Potassium xanthate may be prepared in the following manner: With heating, 300 g. (5.36 moles) of potassium hydroxide is dissolved in 3 l. of absolute ethanol. The solution is then cooled in an ice bath, and the temperature is kept below 10° while carbon disulfide is added in portions with stirring until the solution is no longer alkaline; about 456 g. (360 ml., 5.95 moles) of carbon disulfide is required. The potassium xanthate is collected by suction filtration and air-dried on large sheets of filter paper; yield, 429–472 g. (50–55%).

3. Methods of Preparation

p-Nitrophenyl sulfide has been prepared by the reaction between *p*-chloronitrobenzene and sodium sulfide.¹ This is not a

practical means of preparation, however, because of the variety of substances formed.² The method described has been published.³

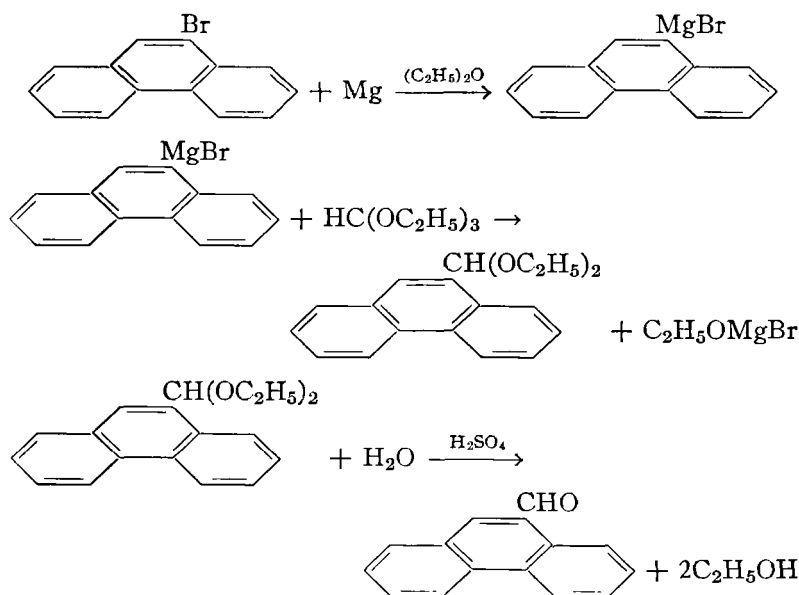
¹ Nietzki and Bothof, *Ber.*, **27**, 3261 (1894).

² Kehrman and Bauer, *Ber.*, **29**, 2362 (1896).

³ Price and Stacy, *J. Am. Chem. Soc.*, **68**, 498 (1946).

PHENANTHRENE-9-ALDEHYDE

(9-Phenanthrenecarboxaldehyde)



Submitted by CLINTON A. DORNFIELD and GEORGE H. COLEMAN.¹

Checked by ROBERT E. CARNAHAN and HOMER ADKINS.

1. Procedure

A dry 5-l. three-necked flask is provided with a stirrer (Note 1), a nitrogen inlet tube, a 500-ml. Pyrex separatory funnel, and a large Allihn reflux condenser. To the upper end of the condenser are attached an outlet tube and a 1-l. separatory funnel. Both separatory funnels and the outlet tube are provided with

calcium chloride drying tubes. To the flask is added 50.3 g. (2.07 gram atoms) of magnesium turnings (Note 2). Nitrogen gas, dried by bubbling through concentrated sulfuric acid, is passed in to displace the air in the flask. The nitrogen atmosphere is maintained until the hydrolysis of the Grignard addition product is completed. Five hundred and fourteen grams (2 moles) of crude 9-bromophenanthrene (p. 19) (Note 3) is melted and poured into the Pyrex separatory funnel (Note 4). One liter of anhydrous ether (dried over sodium wire) is placed in the upper separatory funnel. About 200 ml. of the ether and 10 ml. of the melted bromophenanthrene are allowed to run into the reaction flask. The reaction of the bromophenanthrene with magnesium is initiated by the addition of a few crystals of iodine and 1 ml. of ethyl bromide; the reaction begins after the mixture is stirred for a few minutes without external heating. As the reaction proceeds, the ether and the bromo compound are added at rates sufficient to maintain gentle refluxing. The relative rates of addition should be such that the two separatory funnels will be emptied at about the same time. After the additions are complete, but while the reaction is still in progress, the Grignard reagent begins to precipitate on the sides of the flask. One liter of dry, thiophene-free benzene is added from the Pyrex separatory funnel at such a rate as to keep the Grignard reagent in solution. When refluxing due to the exothermic reaction stops, the mixture is heated at gentle reflux with stirring for 4 hours.

The mixture is allowed to cool until refluxing ceases, and 296.4 g. (2 moles) of ethyl orthoformate (Note 5) is added from the lower separatory funnel over a period of about 30 minutes. The mixture is then refluxed gently for 6 hours.

The reaction mixture is cooled with stirring in an ice bath, and 1 l. of cold 10% hydrochloric acid (Note 6) is added from the separatory funnel; the acid is added dropwise at first and more rapidly after the reaction subsides. The benzene-ether layer is separated from the aqueous layer and concentrated under reduced pressure in a 5-l. round-bottomed flask on a steam bath. One liter of 25% sulfuric acid is added to the residue, and the mixture is refluxed gently for 12 hours.

The mixture is then cooled in an ice bath, the acid is decanted, and the residue is washed twice by decantation with water. The residue is dissolved in 1 l. of benzene in the same flask, and 1.5 l. of water and 1.2 kg. of sodium bisulfite are added. The flask is fitted with a stirrer, and the mixture is stirred vigorously overnight. The mixture is filtered through an 8-in. Büchner funnel, and the bisulfite addition product is washed on the funnel with 500 ml. of benzene.

The filter cake is broken up and returned to the same 5-l. flask. A saturated solution of sodium bicarbonate is added slowly (Note 7) with stirring until there is no further evidence of decomposition. The mixture is stirred for 2 hours longer. The solution is kept alkaline to litmus throughout by the addition of more sodium bicarbonate if necessary. The crude aldehyde is collected on an 8-in. Büchner funnel, washed with water, and allowed to dry as completely as possible. The product is dissolved in 1 l. of chloroform, the small aqueous layer is separated (Note 8), and the solution is dried with Drierite or another suitable drying agent.

A 250-ml. modified Claisen flask, equipped with a dropping funnel, a thermometer, a water-cooled condenser, and a receiver, is arranged for distillation. The chloroform solution is filtered into the dropping funnel, from which it is admitted to the flask slowly as the solvent is distilled (Note 9). When the solvent has been removed, the dropping funnel is replaced by a stopper and the condenser by a 250-ml. distilling flask as a receiver. The residue is distilled at 160–170°/1 mm. The distillate weighs 206–216 g. (50–52%). This material is recrystallized once from glacial acetic acid (approximately 1 g. to 0.9 ml.) and then from ethanol (about 1 g. to 3 ml.) to give 166–174 g. (40–42% over-all yield) of phenanthrene-9-aldehyde melting at 100–101°.

2. Notes

1. A mercury seal may be used, but a glycerol-rubber tube seal² is adequate.
2. The checkers operated on one-fifth the scale specified.

3. Crude bromophenanthrene prepared by the bromination of technical (90%) phenanthrene and purified by distillation only was used by the submitters in this preparation. The anthracene-9-aldehyde, which may be formed from the anthracene present as an impurity in "90% phenanthrene," does not form a sodium bisulfite addition product and so will not contaminate the phenanthrene-9-aldehyde. The checkers used 9-bromophenanthrene, m.p. 54–56° (p. 20), exclusively, but without any advantage in yield. The submitters report yields of 55–60% from pure 9-bromophenanthrene.

4. It is not feasible to add the 9-bromophenanthrene as an ether solution because of the limited solubility of the substance in this solvent. Since the melting point of the crude 9-bromophenanthrene is about 50° it is desirable to heat the melted material to 70° in order to prevent crystallization in the funnel. If the bromo compound begins to solidify in the funnel it may be melted again by careful heating with a micro burner.

5. The ethyl orthoformate should be freshly distilled with rejection of the fraction boiling below 140°.

6. If this procedure is used for the preparation of the acetal instead of the aldehyde, it may be preferable to use ammonium chloride solution for hydrolysis instead of 10% hydrochloric acid.

7. The alkaline solution must be added carefully to avoid excessive foaming.

8. The water in the filter cake is removed with difficulty by drying in air or even in an oven under reduced pressure. If the water is not removed as indicated in the procedure, difficulty may be encountered in the early part of the distillation.

9. The distillation of the solvent may be carried out at reduced pressure if desired.

3. Methods of Preparation

Phenanthrene-9-aldehyde has been obtained by the Sonn and Müller synthesis from 9-phenanthroyl chloride,³ by the Rosenmund reduction of 9-phenanthroyl chloride,⁴ by the Gatterman

hydrogen cyanide synthesis from phenanthrene,⁵ and by the reaction of 9-phenanthrylmagnesium bromide with ethyl formate.⁶ The procedure described above is an adaptation of the method of Miller and Bachman.⁷ This Grignard method has also been used by others.⁸

¹ Work done under contract with the Office of Scientific Research and Development.

² *Org. Syntheses*, **21**, 40 (1941).

³ Shoppee, *J. Chem. Soc.*, **1933**, 40.

⁴ Mosettig and van de Kamp, *J. Am. Chem. Soc.*, **55**, 2996 (1933).

⁵ Hinkel, Ayling, and Beynon, *J. Chem. Soc.*, **1936**, 344.

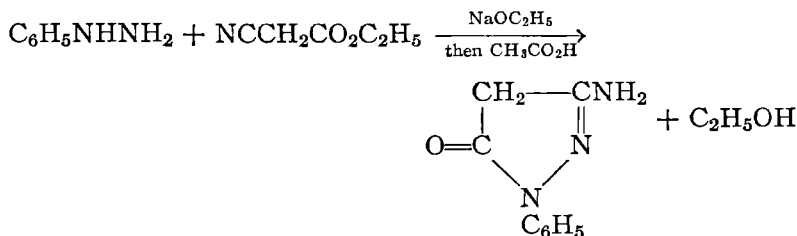
⁶ Bergmann and Israelashwili, *J. Am. Chem. Soc.*, **67**, 1955 (1945).

⁷ Miller and Bachman, *J. Am. Chem. Soc.*, **57**, 768 (1935).

⁸ Hewett, *J. Chem. Soc.*, **1938**, 195; Weizmann, Bergmann, and Berlin, *J. Am. Chem. Soc.*, **60**, 1332 (1938).

1-PHENYL-3-AMINO-5-PYRAZOLONE

(5-Pyrazolone, 3-amino-1-phenyl-)



Submitted by H. D. PORTER and A. WEISSBERGER.

Checked by R. T. ARNOLD and K. MURAI.

1. Procedure

Sodium ethoxide¹ is prepared from 46 g. (2 gram atoms) (Note 1) of sodium and 800 ml. of absolute ethanol in a 2-l. three-necked flask equipped with stirrer and a reflux condenser. To the hot solution is added 113 g. (106 ml., 1 mole) of ethyl cyanoacetate² followed by 108 g. (98 ml., 1 mole) of phenylhydrazine³ (Note 2), and the mixture is stirred and heated in an oil bath at

120° for 16 hours. Then most of the alcohol is removed under reduced pressure and the residue is dissolved in 1 l. of water; the mixture is warmed to about 50° and stirred to facilitate solution. After cooling to room temperature, the solution is extracted with three 100-ml. portions of ether (Note 3). The aqueous phase is acidified by the addition of 100 ml. of glacial acetic acid, cooled in ice, and filtered. The crude product is washed on the filter with 100 ml. of 95% ethanol; it is then transferred to a flask and boiled with 500 ml. of the same solvent, and this mixture is cooled and filtered. The solid is washed with ethanol and dried. The tan crystalline 1-phenyl-3-amino-5-pyrazolone, melting with decomposition at 216–218°, weighs 76–82 g. (43–47%) (Note 4).

2. Notes

1. At least two equivalents of sodium ethoxide are necessary for the reaction, but larger amounts do not improve the yield. Sodium hydroxide in alcohol, or sodamide in benzene, cannot be substituted for the sodium ethoxide solution.

2. All the chemicals used were obtained from the Eastman Kodak Company.

3. Instead of the isolation of the product by concentration, solution in water, and extraction with ether, water may be added directly to the alcoholic solution and the resulting solution acidified. This procedure, however, often leads to a more highly colored product.

4. This material is sufficiently pure for most purposes. If desired, an almost white product may be obtained by two recrystallizations from dioxane (Norite). This treatment entails a 40% loss of the product and raises the melting point by only 2° (to 218–220°).

3. Methods of Preparation

The procedure is essentially that given by Conrad and Zart for the original preparation of the substance,⁴ to which they assigned the incorrect structure of 1-phenyl-3-hydroxy-5-pyrazolone imide.⁵ The compound may also be prepared in about the

same yield by the reaction of phenylhydrazine with ethyl malonate monoimidoester.⁶

The procedure given has been applied with varying success to a number of aromatic and heterocyclic hydrazines.⁷

¹ *Org. Syntheses*, **23**, 18 (1943).

² *Org. Syntheses* Coll. Vol. 1, 254 (1941).

³ *Org. Syntheses* Coll. Vol. 1, 442 (1941).

⁴ Conrad and Zart, *Ber.*, **39**, 2282 (1906).

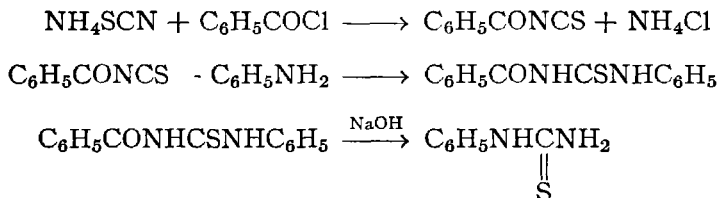
⁵ Weissberger and Porter, *J. Am. Chem. Soc.*, **64**, 2133 (1942).

⁶ Weissberger, Porter, and Gregory, *J. Am. Chem. Soc.*, **66**, 1851 (1944).

⁷ Weissberger and Porter, *J. Am. Chem. Soc.*, **66**, 1849 (1944).

α -PHENYLTHIOUREA

(Urea, 1-phenyl-2-thio-)



Submitted by ROBERT L. FRANK and PAUL V. SMITH.¹

Checked by RICHARD T. ARNOLD and SHERMAN SUNDET.

1. Procedure

In a 500-ml. three-necked flask fitted with a reflux condenser, a mechanical stirrer, and a 100-ml. dropping funnel are placed 17 g. (0.22 mole) of ammonium thiocyanate and 100 ml. of dry acetone (Note 1). Through the dropping funnel is added, with stirring, 28.2 g. (0.2 mole) of benzoyl chloride. After the addition is complete, the mixture is refluxed for 5 minutes. Then a solution of 18.6 g. (0.2 mole) of aniline in 50 ml. of dry acetone is added at such a rate that the solution refluxes gently. The mixture is poured carefully with stirring into 1.5 l. of water, and the resulting yellow precipitate (α -benzoyl- β -phenylthiourea) is sepa-

rated by filtration. The crystals are heated for 5 minutes with a boiling solution of 30 g. of sodium hydroxide in 270 ml. of water. After the removal of a small amount of insoluble material by filtration, the solution is acidified with concentrated hydrochloric acid and then made slightly basic with ammonium hydroxide. Upon standing, the solution deposits the crystalline product. The yield of oven-dried material (m.p. 151–153°) is 25.8 g. (85%). Recrystallization from ethanol yields 23.2 g. (76%) of white plates melting at 152.5–153°.

2. Note

1. The acetone is dried for at least 48 hours over anhydrous calcium sulfate (Drierite) and distilled just before it is used.

3. Methods of Preparation

α -Phenylthiourea has been prepared by the action of ammonium thiocyanate,² thiocyanic acid,³ thiuramdisulfide,⁴ or silicon thiocyanate⁵ on aniline; by the action of ammonium thiocyanate on aniline hydrochloride;⁶ by the action of ammonia on phenyl isothiocyanate,⁷ 1-phenyl-2-thiobiuret,⁸ thiocarbanilide,⁹ phenyldithiocarbamazine,¹⁰ or phenyl isothiocyanate hexasulfide;¹¹ by the addition of hydrogen sulfide to monophenylcyanamide;¹² by the decomposition of salts of phenyldithiocarbamic acid in the presence of lead carbonate,¹³ ammonium polysulfide,¹⁴ or ammonium carbonate;¹⁵ by the reaction of thiophosgene, aniline, and ammonia;¹⁶ and by the action of hydrazine hydrate on phenyldithiobiuret.¹⁷

The preparation of α -phenylthiourea by the procedure described herein has not been reported, although Douglass and Dains¹⁸ have applied the method to the preparation of various substituted phenyl derivatives.

¹ Work done under contract with the Office of Rubber Reserve.

² Schiff, *Ann.*, **148**, 338 (1868); Rathke, *Ber.*, **18**, 3102 (1885).

³ Salkowski, *Ber.*, **24**, 2724 (1891); Challenger and Collins, *J. Chem. Soc.*, **125** 1377 (1924); DeBeer, Buck, Ide, and Hjort, *J. Pharmacol.*, **57**, 19 (1936).

⁴ Klason, *J. prakt. Chem.*, [2] **36**, 57 (1887); Fromm, *Ber.*, **42**, 1955 (1909).

⁵ Reynolds, *J. Chem. Soc.*, **89**, 397 (1906).

⁶ deClermont, *Ber.*, **9**, 446 (1876); Liebermann, *Ann.*, **207**, 122 (1881); Bertram, *Ber.*, **25**, 48 (1892); Ger. pat. 604,639, French pat. 762,310 [*C.A.*, **29**, 819 (1935)]; Krall and Gupta, *J. Indian Chem. Soc.*, **12**, 629 (1935).

⁷ Hofmann, *Compt. rend.*, **47**, 424 (1858); Otterbacher and Whitmore, *J. Am. Chem. Soc.*, **51**, 1909 (1929).

⁸ Birckenbach and Kraus, *Ber.*, **71**, 1492 (1938).

⁹ Gebhardt, *Ber.*, **17**, 3043 (1884); v. Walther and Stenz, *J. prakt. Chem.*, [2] **74**, 223 (1906).

¹⁰ Oliveri-Mandala, *Gazz. chim. ital.*, **51**, II, 195 (1921).

¹¹ Levi, *Gazz. chim. ital.*, **61**, 619 (1931).

¹² Weith, *Ber.*, **9**, 810 (1876).

¹³ Heller and Bauer, *J. prakt. Chem.*, [2] **65**, 365 (1902).

¹⁴ Azzalin, *Gazz. chim. ital.*, **55**, 895 (1925).

¹⁵ Drozdov, *J. Gen. Chem. U.S.S.R.*, **6**, 1368 (1936).

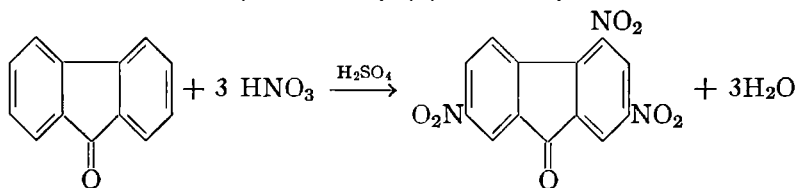
¹⁶ Hutin, *Rev. gén. mat. plastiques*, **7**, 95 (1931).

¹⁷ Fromm, *Ann.*, **426**, 326 (1922).

¹⁸ Douglass and Dains, *J. Am. Chem. Soc.*, **56**, 1408 (1934).

2,4,7-TRINITROFLUORENONE

(Fluorenone, 2,4,7-trinitro-)



Submitted by E. O. WOOLFOLK and MILTON ORCHIN.

Checked by CHARLES C. PRICE and BENJAMIN D. HALPERN.

1. Procedure

In a well-ventilated hood, a 250-ml. dropping funnel, a thermometer, and a mechanical stirrer are connected by ground-glass joints to a 3-l. three-necked round-bottomed flask. Nine hundred milliliters of red fuming nitric acid (sp. gr. 1.59–1.60) is placed in the flask, and 675 ml. of concentrated sulfuric acid (sp. gr. 1.84) is added with stirring. The acid mixture is cooled to 20°, and the cooling bath is removed. A solution of 45 g. (0.25 mole) of

fluorenone (Note 1) in 135 ml. of glacial acetic acid is added dropwise to the mixed acids over a period of about 40 minutes (Note 2). At the end of the addition, the temperature of the reaction mixture is about 45°. The stirrer, thermometer, and funnel are removed, the flask is attached to a reflux condenser with a ground-glass joint, and ground-glass stoppers are placed in the other two openings. The reaction mixture is refluxed for 1 hour and then poured (in the hood) slowly with shaking onto 7 kg. of cracked ice in a 12-l. flask. The product separates as a yellow solid and is filtered by suction and washed with 5 l. of water. The product and 2 l. of water are placed in a 5-l. round-bottomed flask, and steam is passed into the mixture for 1 hour to dissolve and remove acidic impurities (Note 3). The product is filtered by suction, washed with water until the washings are no longer acid to Congo red paper, and air-dried overnight. The material is further dried in a 1-l. round-bottomed flask connected to a water pump and heated in a water bath at 80–90° for several hours. The product is a yellow powder weighing 72–74 g. (91–94%) and melting at 166–171° (Note 4).

The crude product is dissolved in 350 ml. of boiling glacial acetic acid, and the hot solution is filtered by suction (Note 5). Any crystals that separate during the filtration are redissolved by heating the suction flask, and the solution is allowed to cool slowly. The small yellow needles that separate are filtered with suction and washed successively with small quantities of ethanol (30 ml.), water (50 ml.), and ethanol (30 ml.). The yield is 59–61 g. (75–78%) of 2,4,7-trinitrofluorenone, melting at 175.2–176.0°. Additional material can be recovered from the mother liquor by dilution with water, drying the precipitate so formed, and recrystallization from acetic acid. The second crop consists of about 5 g. of pure material, melting at 175.2–176.0°, which usually has a slightly darker color than the first crop.

2. Notes

1. Commercial fluorenone was recrystallized from benzene-ethanol to give material melting at 83–84°. Fluorenone can also

be prepared conveniently from commercial fluorene according to the procedure of Huntress, Hershberg, and Cliff.¹ When the checkers nitrated unrecrystallized commercial fluorenone, m.p. 79–82°, the product obtained (yield 55.5 g.) was of a duller yellow color but melted at 175.5–176.5°.

2. Nitrogen oxides are evolved vigorously if the acetic acid solution of fluorenone is added to the acid mixture too rapidly.

3. If this treatment is omitted the recrystallized product has a brown color which is not removed by repeated recrystallizations.

4. The checkers observed melting points of 165–169° for the crude product.

5. Filter paper is not satisfactory for the filtration of hot acetic acid; a sintered-glass Büchner funnel is recommended.

3. Methods of Preparation

2,4,7-Trinitrofluorenone has been prepared by the nitration of fluorenone,^{2,3} 2,7-dinitrofluorenone,⁴ and 2,5-dinitrofluorenone.⁴ The present method has been published⁵ in connection with reports of the use of the reagent for the conversion of aromatic compounds to solid derivatives.

¹ Huntress, Hershberg, and Cliff, *J. Am. Chem. Soc.*, **53**, 2720 (1931).

² Schmidt and Bauer, *Ber.*, **38**, 3760 (1905). The material reported by these authors as 2,6,7-trinitrofluorenone was subsequently shown to be the 2,4,7-isomer (Bell, *J. Chem. Soc.*, **1928**, 1990).

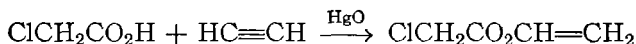
³ Schmidt, Retzlaff, and Haid, *Ann.*, **390**, 231 (1912).

⁴ Ray and Francis, *J. Org. Chem.*, **8**, 58 (1943).

⁵ Orchin, Reggel, and Woodfolk, *J. Am. Chem. Soc.*, **69**, 1225 (1947); Orchin and Woodfolk, *J. Am. Chem. Soc.*, **68**, 1727 (1946).

VINYL CHLOROACETATE

(Acetic acid, chloro-, vinyl ester)



Submitted by RICHARD H. WILEY.

Checked by MAYNETTE VERNSTEN and HOMER ADKINS.

1. Procedure

Vinyl chloroacetate is lachrymatory.

A 1-l. three-necked flask is equipped with an efficient stirrer, a thermometer, a gas inlet tube 10 mm. in diameter, and a reflux condenser. The bulb of the thermometer and the lower end of the gas inlet tube are sufficiently close to the bottom of the flask to be covered by the reactants (Note 1). The upper end of the condenser is attached to a small gas-washing bottle containing enough water so that the rate of passage of the exit gases may be noted. The flask is charged with 200 g. (2.12 moles) of mono-chloroacetic acid, 0.2 g. of hydroquinone, and 20 g. of yellow mercuric oxide (Note 2). A slow stream of acetylene is passed through a spiral trap cooled in Dry Ice-acetone mixture, a mercury safety valve, an empty wash bottle, a sulfuric acid wash bottle, a soda-lime tower, and then into the reaction flask through the gas inlet tube. The stirrer is started, and the contents of the flask are heated gently with steam until the chloroacetic acid just melts (Note 3). The temperature of the reaction mixture is lowered to 40–50° after 30 minutes or as soon as the melting point of the mixture permits the lower temperature to be attained without solidification. An ice bath is used for cooling the mixture when necessary (Note 4). The stirrer is operated fast enough to throw the contents of the flask vigorously against the walls, in order to obtain the most rapid absorption. The absorption of acetylene, very rapid at first, becomes very slow after about 3 hours, and the introduction of the gas is discontinued (Note 5).

The contents of the flask are decanted and filtered or centrifuged to remove as much as possible of the finely divided mercury salt (Note 6). The filtrate is distilled from a Claisen flask, and 117–135 g. of material boiling at 45–55°/20 mm. is collected (Note 7). The distillate is fractionated, and 107–125 g. (42–49%) of vinyl chloroacetate, b.p. 37–38/16 mm., n_D^{25} 1.4422, is collected (Notes 8 and 9).

2. Notes

1. The apparatus is similar to that previously shown¹ except that one of the inlet tubes, T_1 or T_2 , is replaced by a thermometer and the stirrer is equipped with a short sleeve which is connected to the shaft by a rubber tube moistened with glycerol.

2. Merck or Mallinckrodt Reagent grade or Baker C.P. monochloroacetic acid was used without further purification. Distillation of the acid did not improve the yield. Baker or Mallinckrodt yellow mercuric oxide, C.P., was used. The hydroquinone may be added at this point or before the distillation.

3. The submitter suggested that the mixture be heated to 50–55°. The melting point of the chloroacetic acid used by the checkers required that the temperature at the beginning of the reaction be somewhat above 60°. The chief difficulty in carrying out the reaction is due to solidification of chloroacetic acid in the inlet tube if the temperature of the reaction mixture is allowed to fall to the point where the mixture begins to crystallize. If the inlet tube becomes plugged, the pressure in the system will be relieved by the mercury safety valve. The safety valve may consist of a small bottle containing a layer of mercury and carrying a stopper fitted with two glass tubes; one of the tubes, extending just below the stopper, is connected to the acetylene line, and the other, which extends *just* beneath the surface of the mercury, is open to the air.

4. Higher temperatures are said to facilitate the formation of the ethylidene compound. Similar yields have been obtained, however, when the temperature was maintained at 50–55° during the entire reaction period.

5. Addition of more mercuric oxide at this time or after 1½ hours' operation does not affect the rate of absorption or increase the yield. If less than 20 g. of mercuric oxide is used the yield is poorer; for example, an experiment with 10 g. of mercuric oxide resulted in a 37% yield of crude ester.

6. It is difficult to remove the finely divided mercury salt completely by decantation or filtration. All the suspended salt can be removed by centrifuging, but dissolved salt remains and separates from the solution on distillation. The suspended salt does not interfere if the product is distilled rapidly. Long-continued heating of the crude product, such as would be required in a careful fractionation, has resulted in a vigorous decomposition of the mixture.

7. Hydroquinone should be added to the crude ester immediately to stabilize it against polymerization. If to be kept for any length of time before refractionation it should be stored in a cold chest.

8. The submitter observed a somewhat higher boiling point (41–42°/15 mm.) and did not report the refractive index of the product. Both the submitter and checkers used a column 20 cm. in length, 12 mm. in diameter, packed with glass helices, and equipped with a partial take-off head. If the fractionation is carefully conducted, the product is sufficiently pure for most polymerization work. The compound should be stabilized with hydroquinone and stored in a cold chest if it is not to be used immediately.

9. According to the submitter the crude ester may also be purified as follows: The centrifuged reaction mixture is placed in a 1-l. separatory funnel with 500 ml. of ether and washed with 200-ml. portions of a 5% sodium carbonate solution until the unchanged acid is removed. Difficulty with emulsions is sometimes encountered at this point. The ether layer is dried with anhydrous sodium sulfate, and the ether is evaporated on a water bath. The residue is fractionated as above.

3. Methods of Preparation

Vinyl chloroacetate has been prepared from acetylene and chloroacetic acid in the vapor phase at 250° with a zinc-cadmium catalyst,² and in the liquid phase with a mercury salt catalyst.³ The procedure described is an adaptation of that employed by Klatte,⁴ by Skirrow and Morrison,⁵ and by others.⁶

¹ *Org. Syntheses* Coll. Vol. **2**, 363 (1943).

² Hermann, Deutsch, and Baum, U. S. pat. 1,822,525 [*C.A.*, **25**, 5900 (1931)].

³ Ger. pat. 271,381 [*Frdl.*, **11**, 54 (1912-1914)].

⁴ U. S. pat. 1,084,581 [*C.A.*, **8**, 991 (1914)].

⁵ U. S. pat. 1,710,197 [*C.A.*, **23**, 2724 (1929)].

⁶ The preparation of vinyl esters has been reviewed by Ellis, *The Chemistry of Synthetic Resins*, Vol. II, p. 1017, Reinhold Publishing Corporation, New York, 1935.

SUBJECT INDEX

(This cumulative index comprises material from Volumes 20 through 28 of this series, for previous volumes see Collective Volumes 1 and 2.)

Names in small capital letters refer to the titles of individual preparations. A number in ordinary bold-face type denotes the volume. A number in bold-face italics refers to a page which gives preparative directions for substances formed either as principal products or as by-products, numbers in ordinary type indicate pages on which a compound or a subject is mentioned in connection with other preparations. For example, Acetone cyanohydrin, **20, 42, 43**, indicates that acetone cyanohydrin is mentioned on page 42, and that directions for its preparation are given in detail on page 43, of Volume 20.

- Absorbent cotton, **20, 8, 9**
 Acenaphthene, **20, 1; 21, 1, 2; 24, 1**
 ACENAPHTHENEQUINONE, **24, 1**
 ACENAPHTHENOL-7, **21, 1**
 ACENAPHTHENOL ACETATE, **21, 1**
 Acenaphthenone, **21, 3**
 β -3-ACENAPHTHENYLCARBONYLPROPIONIC ACID, **20, 1**
 β -(1-ACENAPHTHOYL)-PROPIONIC ACID, **20, 4**
 β -(3-ACENAPHTHOYL)-PROPIONIC ACID, **20, 1**
 Acetal, **23, 8; 25, 1**
 ethyl formate method, **25, 93**
 Acetaldehyde, **23, 61, 84; 24, 62; 27, 24; 28, 28**
 ACETALDEHYDE, AMINO-, DIETHYL ACETAL, **24, 3**
 ACETALDEHYDE, BROMO-, DIETHYL ACETAL, **23, 8, 24, 3**
 Acetamide, **25, 36**
 p -ACETAMINOBENZENESULFINATE, SODIUM, **22, 31**
 α -Acetamino-3,4-methylenedioxycinnamic acid, **22, 93**
 Acetanilide, **28, 26**
 ACETANILIDE, α -BENZOYL, **25, 7**
 ACETANILIDE, p -CHLOROACETYL, **28, 26**
 Acetic acid, **22, 57, 87; 23, 37; 24, 76; 28, 63, 92**
 ACETIC ACID, AMINOXY-, HYDROCHLORIDE, **27, 15**
 ACETIC ACID, BENZOYL-, ETHYL ESTER, **23, 35; 25, 7**
 ACETIC ACID, BROMO-, ETHYL ESTER, **23, 37**
 ACETIC ACID, CHLORO-, VINYL ESTER, **28, 94**
 ACETIC ACID, DI-(p -CHLOROPHENYL), **26, 21**
 Acetic anhydride, **20, 6, 55, 75, 102; 21, 13, 105, 22, 1, 54, 56, 91; 23, 37, 64; 24, 18, 76, 85; 25, 78; 27, 38; 28, 1, 3, 60, 63, 68, 70**
 ACETOACETANILIDE, **21, 4; 24, 68**
 ACETOBROMOGLUCOSE, **22, 1; 25, 53**
 Acetone, **20, 6, 8, 40, 43, 62; 22, 101; 23, 66, 79, 26, 38; 28, 49, 73**
 drying, **20, 7; 25, 54**
 pyrolysis to ketene, **21, 64, 65**
 "Acetone-anil," **28, 49**
 Acetone carboxymethoxime, **27, 15**
 Acetone cyanohydrin, **20, 42, 43**
 Acetonitrile, **24, 6**
 ACETONITRILE, DIETHYLAMINO-, **27, 20**
 ACETONITRILE, DIPHENYL-, **28, 55**
 Acetophenone, **20, 32; 21, 39; 22, 99; 23, 30, 48, 68; 24, 9, 82**
 ACETOPHENONE, 2, 4-DIHYDROXY-, **21, 103**
 ACETOPHENONE, 2,5-DIHYDROXY-, **28, 42**
 Acetophenoneoxime, **22, 27**
 ACETOPHENONEPHENYLHYDRAZONE, **22, 98, 99**
 2-ACETOTHIEONE, **28, 1**
 Acetoxime, **27, 15, 17**
 1-ACETOXY-3-NAPHTHALDEHYDE, **21, 87**
 Acetylacetaldehyde, **27, 93**
 ACETYLACETONE, **20, 6; 21, 68**
 copper salt, **20, 6**
 Acetylation, **20, 21, 74**
 of an amine in aqueous solution, **25, 78**
 of fluorene, **28, 3**
 of gentiobiose, **22, 54**
 of glucose, **22, 1**
 of thiophene, **28, 1**
 of 6-trityl- β -D-glucose, **22, 56**
 ACETYLBENZYL, **23, 1**
 Acetyl bromide, **23, 102**
 Acetyl chloride, **20, 21; 21, 46; 23, 100, 103, 105; 24, 41**
 Acetylene, **20, 40, 22, 101; 28, 94**
 2-ACETYLLUORENE, **28, 3, 63**

- N-Acetylising, **28, 70**
 ACETYLKETENE, **21, 64**
 9-ACETYLPHENANTHRENE, **28, 6**
 Acetylsalicylyl chloride, **23, 66**
 Acetylsalicylyl peroxide, **23, 66**
 Acetyl-*o*-toluidine, **22, 94**
 substituted, conversion to indoles, **22, 95**
 Acetylxylinides, conversion to indoles, **22, 95**
 ACRIDINE, 5-(9-)-AMINO-, **22, 5**
 Acridone, **25, 5**
 Acrolein, **25, 1**
 ACROLEIN, DIETHYL ACETAL, **25, 1**
 Acrylates, **26, 20**
 ACRYLIC ACID, *n*-BUTYL ESTER, **26, 18**
 ACRYLIC ACID, α,β -DIBROMO- β -FORMYL-, **27, 60**
 Acrylic esters, **26, 20**
 Acrylonitrile, **27, 3**
 Acylation by an ester, **23, 35; 28, 44**
 Acylchlororesorcinols, **20, 58**
 Acylresorcinols, **20, 58**
 Adapter for steam distillation, **22, 11**
 Addition, of ammonia to acrylonitrile, **27, 3**
 of bromine to a double bond, **22, 50; 23, 9; 24, 33; 27, 76**
 of bromine to an unsaturated acid, **22, 76, 82**
 of bromine to an unsaturated aldehyde, **25, 92**
 of bromine to an unsaturated ester, **27, 76**
 of bromine to an unsaturated ketone, **27, 5**
 of a carboxylic acid to acetylene, **28, 94**
 of chlorine to aromatic iodo compounds, **22, 69, 70**
 of a cyanide to a lactone, **22, 30**
 of cyanoacetate to *p*-benzoquinone, **26, 25**
 of ethanol to acrolein, **25, 1**
 of a Grignard reagent to a nitrile, **28, 6**
 of hydrogen bromide to ethyl acrylate, **20, 65**
 of hydrogen bromide to methyl acrylate, **20, 64**
 of hydroxylamine to cinnamic acid, **22, 26**
 of a lithium aryl to an aldehyde, **23, 84**
 of a lithium aryl to ethylene oxide, **23, 85**
 of methylamine to ethyl acrylate, **20, 36**
 of methylamine to mesityl oxide, **25, 28**
 of methylamine to methyl acrylate, **20, 37**
 of phenylhydrazine to carbon disulfide, **25, 38**
- Addition—*Continued*
 of phenylmagnesium bromide to phthalide, **27, 30**
 Addition tube, **20, 21**
 Adipyl chloride, **26, 58**
 bromination of, **26, 58**
 Air trap, **23, 42**
 Alanine, **23, 15**
 β -ALANINE, **27, 1**
 ALANINE, β -(3,4-DIHYDROXYPHENYL)-*N*-METHYL-, **22, 89, 91**
dl-ALANINE, α -PHENYL-, **24, 9**
 Alcoholic hydrochloric acid, **22, 77, 83**
 standardization, **22, 80**
 Alcoholysis, **20, 67**
 of dibromoethyl acetate, **23, 8**
 of esters, **26, 19**
 of polylactic acid, **26, 4**
 Aldehyde synthesis, **20, 14; 28, 83**
 from acid chlorides by Rosenmund reaction, **21, 84, 87, 88, 110**
 Gattermann, **23, 57**
 ALDEHYDOACID, **23, 76; 27, 60**
 Alkoxyanilines, **25, 10**
 Alkoxynitrobenzenes, **25, 10**
 2-Alkylaminoethanols, **26, 39**
 Alkylation, of alkylidenecyanoacetic esters, **25, 46**
 of cyclohexanone, **28, 8**
 of ethyl acetoacetate, **27, 35**
 of nitrophenols, **25, 9**
 of thiourea, **22, 59**
 use of boron fluoride, **27, 35**
 Alkylchlororesorcinols, **20, 59**
 Alkylene bromide, **20, 24**
 Alkylene thioureas, **26, 35**
 Alkylidenecyanoacetic esters, **25, 48**
 Alkyl lactate, **26, 6**
 Alkyl phenyl selenides, **24, 91**
 S-ALKYLTHIURONIUM HALIDES, **22, 60**
dl-ALLOTHREONINE, **20, 104**
 ALLOXAN, **23, 3**
 DIHYDRATE, **23, 3, 6**
 MONOHYDRATE, **21, 5**
 TETRAHYDRATE, **23, 3**
 Allyl alcohol, **26, 4**
 Allyl bromide, **25, 49; 28, 8**
 Allyl chloride, **24, 97; 27, 7**
 Allyl cyanide, **24, 96, 97**
 2-ALLYLCYCLOHEXANONE, **28, 8**
 Allyl ether, **26, 5**
 ALLYL LACTATE, **26, 4**
 Alumina, activated, **23, 25**
 regeneration of, **23, 25**
 Aluminum, commercially pure (2S), **21, 9**
 Aluminum alloy (17ST), **21, 9**
 ALUMINUM *tert*-BUTOXIDE, **21, 8, 18, 39**
 Aluminum chloride, **20, 1, 29**
 anhydrous, **21, 25; 23, 57, 102; 24, 26, 70; 28, 3, 26, 42, 56**

- Aluminum ethoxide, **21, 9**
 Aluminum isopropoxide, **21, 9**
 AMALGAMATED ZINC, **20, 57; 23, 86**
 Amide, **20, 37, 62, 66; 25, 58, 71**
 from an acid and urea, **25, 95**
 preparation by ammonolysis, **20, 62**
 Amination, by reduction of a ketone in
 the presence of ammonia, **23, 68**
 of bromoacetal with use of high-pres-
 sure hydrogenation bomb, **24, 3**
 of α -bromoisocaproic acid, **21, 75**
 of α -bromo- β -methylvaleric acid, **21,**
 62
 of α -bromo- β -phenylpropionic acid,
 21, 101
 of 4-bromo-*o*-xylene, **28, 46**
 of 3-hydroxy-2-naphthoic acid, **22, 19**
 of α -nitronaphthalene, **28, 80**
 with hydroxylamine, **28, 80**
 AMINOACETAL, **24, 3**
 Aminoacetic acid, **22, 59**
 Amino acid, **20, 81, 101; 22, 13, 23, 26,**
 59, 90, 93; 24, 9
 9-AMINOACRIDINE, **22, 5**
 basic strength of, **22, 8**
 9-Aminoacridine hydrochloride, fluores-
 cence of, **22, 7**
 9-Aminoacridines, substituted, **22, 7**
o-AMINO BENZALDEHYDE, **28, 11**
m-AMINO BENZALDEHYDE STANNICHO-
 RIDE, **25, 55**
p-Aminobenzoic acid, **25, 86**
 2-Aminobenzothiazole, **22, 18**
o-AMINO BENZYL ALCOHOL, **21, 10**
 α -AMINO BENZYL CYANIDE, **22, 23, 25**
 2-Amino-1-butanol, N-alkyl derivative,
 26, 39
 2-AMINO-*p*-CYMENE, **22, 9**
 α -AMINODIETHYLACETIC ACID, **22, 13**
 4-AMINO-2,6-DIMETHYLPYRIMIDINE, **24, 6**
 α -AMINO- α -ETHYL BUTYRIC ACID, **22, 13**
 AMINO GUANIDINE BICARBONATE, **26, 7,**
 11
 Aminoguanidine sulfate, **26, 12**
 2-AMINOHEPTANE, **23, 70**
dl- β -AMINOHYDROCINNAMIC ACID, **22, 26**
 α -AMINOISOVALERIC ACID, **20, 106**
 Aminolysis of phenyl salicylate, **26, 92**
 2-AMINO-6-METHYLBENZOTHAZOLE, **22,**
 16
 1-Amino-2-methyl-2-propanol, N-alkyl
 derivatives, **26, 39**
 2-Amino-2-methyl-1-propanol, **27, 12**
 α -AMINO- β -METHYLVALERIC ACID, **21, 60**
 3-AMINO-2-NAPHTHOIC ACID, **22, 19; 27,**
 47
 1-Amino-2-naphthol-4-sulfonic acid, **21,**
 91, 94
 2-AMINO-4-NITROPHENOL, **25, 5**
 2-Amino-5-nitrotoluene, **20, 73; 22, 44**
dl- α -AMINOPHENYLACETIC ACID, **22, 23**
p-AMINOPHENYL DISULFIDE, **28, 14**
dl- α -AMINO- α -PHENYLPROPIONIC ACID,
 24, 9
dl- α -AMINO- β -PHENYLPROPIONIC ACID,
 21, 99
dl- β -AMINO- β -PHENYLPROPIONIC ACID,
 22, 26
 1-Amino-2-propanol, N-alkyl deriva-
 tives, **26, 39**
 2-Amino-1-propanol, N-alkyl deriva-
 tives, **26, 39**
 3-Amino-1-propanol, N-alkyl deriva-
 tives, **26, 39**
 β -AMINOPROPIONITRILE, **27, 1, 3**
 2-Aminopyridine, **26, 16**
 Amino sugar, **26, 36**
p-Aminothiophenol, sodium salt, **28, 14**
 2-Amino-*p*-toluic acid, **27, 47**
 3-AMINO-1,2,4-TRIAZOLE, **26, 11**
 4-AMINO-1,2,4-TRIAZOLE, **24, 12**
 hydrochloride, **24, 13**
 5(3)-Amino-1,2,4-triazole carboxylic
 acid-3(5), **26, 12**
 Ammonia, **20, 87; 22, 19; 23, 14; 27, 58,**
 73; 28, 46
 alcoholic, **23, 23**
 chloroform solution of, **22, 6**
 liquid, **20, 62; 21, 70, 71; 23, 20, 68,**
 71; 24, 3; 25, 25; 28, 8, 44
 action on a copper safety disk, **23,**
 70
 introduction into a bomb, **23, 69, 71**
 methanolic, **23, 72**
 Ammonium acetate, **25, 46**
 Ammonium carbonate, **20, 42; 22, 6**
 Ammonium chloride, **22, 13, 23; 24, 9**
 Ammonium dithiocarbamate, **27, 73**
 Ammonium hydroxide, **27, 3**
 Ammonium thiocyanate, **28, 89**
 Ammonolysis, **20, 62**
n-Amyl alcohol, **26, 83; 27, 76**
n-Amyl cyanide, **23, 72**
 Amylene, **22, 82**
 α -Amylhexyldimethylamine, **25, 91**
 Analysis of iodoso and iodoxy com-
 pounds, **22, 71, 72, 73, 74**
 ANHYDRIDES, ACID, **26, 1**
 Anilide from an ester, **25, 7**
 Aniline, **21, 4; 25, 7; 26, 41; 28, 49, 89**
 ANILINE, N,N-DIMETHYL-*m*-NITRO-, **27,**
 62
 ANILINE, *p,p'*-DITHIODI-, **28, 14**
 ANILINE, *p,p'*-SULFONYLBIS-, **22, 31**
o-Anisidine, **25, 24**
p-Anisidine, **25, 78**
p-ANISIDINE, 2-NITRO-, **25, 78**
 Anisoyl chloride, **23, 66**
 ANISOYL PEROXIDE, **23, 66**
 Anthracene, **20, 11**
 9-ANTHRALDEHYDE, **20, 11**
 ANTHRANILALDEHYDE, **28, 11**

- Anthranilic acid, **21, 10; 27, 45**
 ANTHRAQUINONE, 2,3-DIMETHYL-, **22, 37**
 Antioxidant, **20, 65**
 Apparatus, adapter for steam distillations, **22, 10, 11**
 automatic water trap for azeotropic distillation, **23, 38; 25, 42, 46**
 bain-marie ware, **25, 72, 97**
 Claisen flask modified with column, **22, 11**
 continuous extractor, **23, 49; 28, 66**
 enameled steel pots, **25, 72, 97**
 for absorption of gases, **23, 48**
 for adding a solid without exposure to air, **23, 59, 102**
 for catalytic dehydration, **22, 40**
 for chlorination under slight pressure, **25, 14, 22**
 for distillation of solids, **20, 20**
 for fractional distillation, **20, 26, 52, 96; 25, 1**
 for generating dry methylamine, **20, 35**
 for heating under pressure, **20, 85**
 for introduction of bromine in a current of air, **23, 9, 75**
 for manipulation of liquid ammonia, **23, 21**
 for partial condensation during distillation, **20, 26, 27**
 for preparation of sodamide, **20, 87**
 for removal of water from reaction mixture, **28, 74**
 for steam distillation, **20, 2**
 shaking extractor, **23, 78**
 spray trap, **23, 1**
d-ARABINOSE, **20, 14**
d-ARABINOSEDIIPHENYLHYDRAZONE, **20, 15**
 Arsenic oxide, **27, 48**
 Arsenious oxide, **26, 61**
 Arylarsonic acids, **26, 62**
 Arylmethylcarbinols, **28, 28, 30, 31, 32**
 Asbestos fiber mat for Büchner funnel, **25, 57**
 Autoclave, **20, 82, 85, 102; 21, 72**
 stirring, **22, 20**
 use of hydrogenation bomb as, **21, 68; 22, 20**
 cleaning, **22, 21**
 Autooxidation, **22, 81, 85**
 Azeotrope, of allyl alcohol, water, and benzene, **26, 5**
 of methyl alcohol and methyl acrylate, **26, 19**
 Azeotropic distillation, **20, 66, 106; 23, 38**
 Azide, formation from a hydrazine, **22, 96**
 AZOBENZENE, **22, 28**
 AZOYL CHLORIDE, **25, 87**
 Azulene, removal from a hydrocarbon, **24, 86**
 Bain-marie ware, **25, 72, 97**
 Barbier-Wieland, degradation of carboxylic acid by method of, **24, 38, 41**
 Barbituric acid, **21, 5**
 Barium carbonate, **22, 86**
 Barium chloride, **23, 17**
 Barium hydroxide, **22, 87, 91; 25, 75; 27, 1**
 Barium malonate, **23, 17**
 Barostat, **23, 46, 47**
 Bayberry wax, **20, 67**
 Benzalacetone, **27, 5**
 BENZALACETONE DIBROMIDE, **27, 5, 9**
 Benzalacetophenone dibromide, **27, 11**
 BENZALBARBITURIC ACID, **21, 5**
 Benzaldehyde, **21, 5, 51, 108; 22, 24**
 determination of acid content, **25, 43**
 BENZALDEHYDE, *m*-HYDROXY-, **25, 55**
 BENZALDEHYDE, *o*-NITRO-, **24, 75**
 BENZALMALONIC ESTER, **25, 42**
 Benzalphenalide, **27, 31**
 Benzene, dry, thiophene-free, **23, 95, 97, 102, 103; 26, 2; 28, 56**
 use in azeotropic esterification, **23, 38; 24, 72; 26, 5**
 BENZENEARSONIC ACID, *p*-NITRO-, **26, 60**
 BENZENE, BUTYL-, **25, 11**
p-BENZENEDIACETIC ACID, 2,5-DIHYDROXY-, **26, 24**
 BENZENE, IODO-, DICHLORIDE, **22, 69**
 BENZENE, IODOSO-, **22, 70**
 BENZENE, IODOXY-, **22, 72, 73**
 BENZENE, 1-METHOXY-2-PHENOXY-, **26, 50**
 BENZENE, 1,3,5-TRIACETYL-, **27, 91**
 BENZENE, TRIAZO-, **22, 96**
 Benzil, **20, 48; 23, 92**
 BENZILMONOHYDRAZONE, **20, 47, 48**
 Benzohydril benzoate, **24, 55**
 Benzoic acid, **21, 27; 22, 48, 49**
 BENZOIC ACID, 2,5-DINITRO-, **22, 44**
 BENZOIC ACID, 3,5-DINITRO-, **22, 48, 49**
 BENZOIC ACID, *p*-PHENYLAZO-, **25, 86**
 BENZOIC ANHYDRIDE, *p,p'*-DICHLORO-, **26, 1**
 Benzoin, **23, 86**
 BENZONITRILE, 2,6-DIMETHOXY-, **22, 35**
 Benzophenone, **23, 99**
 Benzophenone azine, **24, 55**
 Benzophenone hydrazone, **24, 54**
 1,2-BENZOPYRAN-3-CARBOXYLIC ACID, 2-oxo-, ethyl ester, **28, 24**
 BENZOPYRROLE, **23, 42**
 BENZO(*ij*)QUINOLIZINE, 1,2,3,5,6,7-HEXAHYDRO-, **26, 40**
p Benzoquinone, **26, 25**
 BENZOTHAZOLE, 1-AMINO-5-METHYL-, **22, 16**
 BENZOTHAZOLE, 2-AMINO-6-METHYL-, **22, 16**
 1,2,3-BENZOTRIAZOLE, **20, 16**

- BENZOYLACETANILIDE, **25, 7**
 BENZOYLACETIC ESTER, **23, 35**
 Benzoylation of acetoacetic ester by ethyl benzoate, **23, 35**
 Benzoyl chloride, **24, 14; 28, 16, 89**
 purification of, **24, 15**
 BENZOYL CHLORIDE, *p*-PHENYLazo-, **25, 87**
 BENZOYL CYANIDE, **24, 14, 16**
 BENZOYL DISULFIDE, **28, 16**
 BENZOYLFORMIC ACID, **24, 16**
 α -Benzoyl- β -phenylthiourea, **28, 89**
 Benzoyl-*o*-toluidines, conversion to indoles, **22, 95**
 Benzoylxyldines, conversion to indoles, **22, 95**
 Benzyl alcohol, **23, 14**
 BENZYL ALCOHOL, *m*-CHLORO- α -METHYL-, **28, 28, 31**
 Benzylamine, methylation of, **25, 91**
 BENZYLAMINE, α -METHYL-, **23, 68**
 BENZYL CARBAMATE, **23, 14**
 Benzyl chloride, **21, 99**
 BENZYL CHLOROFORMATE, **23, 13**
 BENZYL CHLOROMETHYL KETONE, **26, 13**
 Benzyl cyanide, **23, 71; 25, 25; 28, 55**
 Benzyl dodecylmethylamine, **25, 91**
 Berthelot tubes, **26, 66**
 BIALLYL, **27, 7**
 Bisulfite compound, use for purification of an aldehyde, **23, 78; 28, 85**
 use for purification of alkylidenecyanoacetic esters, **25, 47**
 use for purification of a ketone, **23, 79**
 Blanc reaction, **20, 59; 24, 30; 25, 65**
 Blood, defibrinated, **21, 53**
 Booster pump, use of, for hydrogenation, **23, 69**
 Boron trifluoride, **20, 6; 27, 35**
 Bottles for pressure reactions, **27, 4**
 Bromination, **20, 18, 81, 92, 101**
 of acetic acid, **23, 37**
 of 2-aminopyridine, **26, 16**
 of benzyl cyanide, **28, 55**
 of furoic acid, **27, 60**
 of a lactone, phthalide, **23, 74**
 of phenanthrene, **28, 19**
 of sulfanilamide by hydrogen peroxide and hydrobromic acid, **24, 48**
 of *o*-xylene, **28, 22**
 Bromine, **20, 18, 23, 81, 92, 101; 21, 61, 93; 22, 50, 76, 82; 25, 92; 27, 6, 54, 60, 76; 28, 19, 22, 55**
 dry, **20, 93, 106, 108; 21, 74, 101; 23, 9, 37, 74, 94; 24, 33; 26, 53**
 BROMOACETAL, **23, 8, 45; 24, 3**
 BROMOACETIC ACID, **23, 37**
 3-Bromo-4-aminotoluene, **23, 11**
m-BROMOANILINE, **23, 12; 24, 24**
o-Bromoanisole, **24, 24**
 α -BROMOBENZALACETONE, **27, 9**
 α -Bromobenzalacetophenone, **27, 10**
 Bromobenzaldehydes, **28, 30**
 Bromobenzene, **21, 79; 23, 83, 93, 98; 24, 42, 85, 89; 25, 11; 26, 50; 27, 30**
p-Bromobenzoyl chloride, **23, 66**
p-BROMOBENZOYL PEROXIDE, **23, 66**
 γ -Bromobutyronitrile, **23, 22**
m-Bromochlorobenzene, **28, 28**
 α -BROMOCINNAMIC ALDEHYDE, **25, 92**
 α -BROMOCINNAMIC ALDEHYDE ACETAL, **25, 92**
o-BROMO-*p*-CRESOL, **23, 11**
 Bromocyclohexane, **25, 26**
 ω -Bromo esters, by bromination of silver salt, **26, 54**
 1-BROMO-2-ETHOXYETHANE, **23, 32**
 3-BROMO-4-HYDROXYTOLUENE, **23, 11**
 α -BROMOISOCAPROIC ACID, **21, 74**
 α -BROMISOVALERIC ACID, **20, 106**
 Bromomesitylene, **21, 77**
 α -BROMO- β -METHOXY-*n*-BUTYRIC ACID, **20, 101**
 α -BROMO- β -METHOXYPROPIONIC ACID, **20, 82**
 3-Bromo-4-methoxytoluene, **26, 51**
o-Bromo-*p*-methylanisole, **23, 12**
 α -BROMO- β -METHYLVALERIC ACID, **21, 61**
 α -Bromonaphthalene, **21, 89**
 6-BROMO-2-NAPHTHOL, **20, 18**
 9-BROMOPHENANTHRENE, **28, 19, 34**
m-Bromophenol, **23, 12**
 α -Bromophenylacetone, **28, 55**
 Bromophenylmethylcarbinols, **28, 30**
 α -BROMO- β -PHENYLPROPIONIC ACID, **21, 100**
p-Bromophenylselenophenol, **24, 91**
 2-BROMOPHTHALIDE, **23, 74**
 β -Bromopropionic acid, **20, 65**
 γ -Bromopropylphthalimide, **24, 44, 46**
N-(γ -Bromopropyl)-tetrahydroquinoline, **26, 41**
 2-BROMOPYRIDINE, **26, 16**
 Bromostyrenes, **28, 33**
 3-Bromosulfanilamide, **24, 51**
 4-BROMO-*o*-XYLENE, **23, 22, 46**
 1,3-BUTADIENE, 2,3-DIMETHYL-, **22, 39, 40**
 2-BUTANONE, 3,4-DIBROMO-4-PHENYL-, **27, 5**
 2-BUTENE-1,4-DIONE, 1,4-DIPHENYL-, **20, 29**
 β -BUTENOIC ACID, **24, 96**
 3-BUTEN-2-ONE, 3-BROMO-4-PHENYL-, **27, 9**
 3-BUTENONITRILE, **24, 97**
m-n-Butoxyaniline, **25, 10**
p-n-Butoxyaniline, **25, 10**
m-n-Butoxynitrobenzene, **25, 10**
o-n-BUTOXYNITROBENZENE, **25, 9**
tert.-BUTYL ACETATE, **20, 21**
 acetic anhydride method, **24, 18**
 acetyl chloride method, **24, 19**

- n*-BUTYL ACRYLATE, **26, 18**
n-Butyl alcohol, **23, 43; 26, 19**
tert.-Butyl alcohol, **20, 21; 21, 8, 39; 23, 42; 24, 18, 19, 20, 21**
 anhydrous, **23, 46**
n-Butylamine, methylation of, **25, 91**
tert.-BUTYLAMINE, **27, 12**
n-BUTYLBENZENE, **25, 11**
n-Butyl bromide, **25, 9**
sec.-Butyl bromide, **21, 60**
n-Butyl β -bromopropionate, **26, 21**
p-*tert.*-Butylcatechol, **28, 31, 32**
tert.-Butyl chloroacetate, **24, 21**
n-Butyl- β -chloropropionate, **26, 21**
tert.-Butyl cinnamate, **24, 21**
n-Butyl α, β -dibromopropionate, **26, 21**
tert.-Butyl isobutyrate, **24, 20**
tert.-Butyl isovalerate, **24, 21**
sec.-BUTYLMALONIC ACID, **21, 61**
n-Butyl nitrite, **24, 25**
m-*tert.*-Butylphenylmethylcarbinol, **28, 30**
tert.-Butyl propionate, **24, 20**
 1-*n*-BUTYLPYRROLIDINE, **25, 14**
n-Butylselenol, **24, 91**
n-BUTYL *p*-TOLUENESULFONATE, **20, 51**
 3-BUTYN-2-OL, 2-METHYL-, **20, 40**
 Butyraldehyde, **26, 31**
n-Butyric anhydride, **21, 14**
 Butyrylchlororesorcinol, **20, 58**
o-Butyrylphenol, **20, 58**
p-Butyrylphenol, **20, 58**
- Cadmium alkyl, **28, 75, 79**
 Cadmium chloride, **28, 75**
 Calcium carbonate, **22, 54**
 Calcium chloride, **23, 103**
n-Caproic acid, **21, 13**
 CAPROIC ACID, α -CYANO-, ETHYL ESTER, **26, 31**
n-CAPROIC ANHYDRIDE, **21, 13**
 Capronitrile, **26, 33**
 Caproylchlororesorcinol, **20, 58**
o-Caproylphenol, **20, 58**
p-Caproylphenol, **20, 58**
 Caproylresorcinol, **20, 58**
 CAPRYLIC ACID, ζ -METHYL- γ -OXO-, METHYL ESTER, **28, 75**
 3-CARBETHOXYCOUMARIN, **28, 24**
 ω -Carbethoxynonanoyl chloride, **28, 79**
 ω -Carbethoxypelargonyl chloride, **25, 21**
 δ -Carbethoxyvaleryl chloride, **25, 21; 28, 79**
 CARBINOL, TRIPHENYL-, **23, 98**
 CARBINOL, TRIS-(4-PHENYLPHENYL)-, **23, 95, 97**
 Carbitol, **22, 32**
 CARBOBENZOXALANINE, **23, 15**
 CARBOBENZOXYCHLORIDE, **23, 13**
 CARBOBENZOXYGLYCINE, **23, 14**
- ω -CARBOMETHOXYPELARGONYL CHLORIDE, **25, 71**
 β -CARBOMETHOXYPROPIONYL CHLORIDE, **25, 19; 28, 76, 78**
 Carbon dioxide, **23, 74**
 solid (Dry Ice), **21, 71, 77; 22, 101**
 Carbon dioxide atmosphere, **22, 78, 84, 91**
 Carbon disulfide, **21, 81; 25, 38; 28, 3, 26, 82**
 precautions in use of, **28, 3, 26**
 reaction with ammonia, **27, 73**
 reaction with ethylene diamine, **26, 34**
 Carbon tetrachloride, **23, 102**
 Carborundum crystals, **20, 96**
 as column filling, **22, 39; 23, 22**
 CARBOSTYRIL, 4-METHYL-, **24, 68**
 Carboxyaldehyde, **23, 76**
 N-CARBOXYANTHRANILIC ANHYDRIDE, **27, 45**
o-CARBOXYBENZYL CYANIDE, **22, 30**
 CARBOXYMETHOXYLAMINE HEMIHYDROCHLORIDE, **27, 15**
o-CARBOXYPHENYLACETONITRILE, **22, 30, 61**
 Caro's acid, **22, 44, 74**
 CARVACRYLAMINE, **22, 9**
 Catalyst, alumina, **22, 40**
 boron trifluoride, **20, 6**
 copper bronze, **20, 45**
 copper-chromium oxide for decarboxylation, **22, 67**
 copper oxide for decarboxylation, **22, 67**
 cupro-cupri sulfite, **28, 53**
 hydrobromic acid, **22, 39**
 hydrogenation, Universal Oil Products, **27, 22**
 in bromination, **28, 22**
 in ester interchange, **26, 19**
 mercuric oxide, **28, 94**
 palladium-barium sulfate, **21, 85, 110; 26, 77**
 palladium-carbon, **26, 78**
 phosphoric acid, **28, 1**
 piperidine acetate, **28, 24**
 piperidine benzoate, **25, 42**
 poison, for use in Rosenmund reduction, **21, 85, 87**
 pyridine, **25, 51**
 sodium bicarbonate, **20, 26**
 sulfuric acid, **22, 1**
 zinc chloride, **28, 60**
- CATALYST, RANEY NICKEL, **21, 15, 108; 22, 9, 12; 23, 68, 71, 90; 25, 10**
 estimation of quantity of, **21, 17**
 storage under alcohol, dioxane, and methylcyclohexane, **21, 16**
 Cellosolve, **23, 32**
 Centrifuge, **22, 77, 83**
 Cerelease, **22, 2**
 Chitin, **26, 36**

- Chloral hydrate, **20, 37**
 Chlorination, of a ketone, **23, 48; 25, 22**
 of secondary amines, **25, 14**
 of sulfanilamide by hydrogen peroxide and hydrochloric acid, **24, 47**
 Chlorine, **22, 69; 23, 48; 25, 14, 22**
 Chloroacetal, **24, 5**
 Chloroacetic acid, **23, 53; 28, 94**
 drying, **23, 54**
 Chloroacetone, **25, 36**
p-CHLOROACETYLACETANILIDE, **28, 26**
 Chloroacetyl chloride, **24, 21, 26; 28, 26**
 9-CHLOROACRIDINE, **22, 6, 7**
 N-Chloroamines, **25, 14**
 cyclization to N-alkylpyrrolidines, **25, 19**
m-Chloroaniline, **24, 24**
o-Chloroaniline, **24, 22**
p-Chloroaniline, **28, 14**
o-Chlorobenzaldehyde, **28, 30**
p-Chlorobenzaldehyde, **28, 30**
 Chlorobenzene as a solvent, **22, 16**
p-Chlorobenzoic acid, **26, 2**
p-CHLOROBENZOIC ANHYDRIDE, **26, 1**
p-Chlorobenzoyl chloride, **26, 2**
 4-Chlorobiphenyl, **23, 95, 97**
m-Chlorobromobenzene, **24, 24**
o-CHLOROBROMOBENZENE, **24, 22**
 γ -Chlorobutyronitrile, **23, 20; 24, 36**
 2-CHLOROCYCLOHEXANONE, **25, 22**
 Chloroform, **22, 35, 57, 63, 71**
 anhydrous, **22, 69**
 7-Chloro-4-hydroxy-3-quinolinecarboxylic acid, **28, 39**
 α^2 -CHLOROISODURENE, **25, 65**
 ω -CHLOROISONITROSOACETOPHENONE, **24, 25**
 2-CHLOROLEPIDINE, **24, 28; 26, 45**
 Chloromethylation, **20, 59; 24, 30; 25, 65**
 Chloromethyl ketones, **26, 14**
 1-CHLOROMETHYLNAPHTHALENE, **24, 30**
bis-(Chloromethyl)-naphthalene, **24, 31**
 α -Chloronaphthalene, **21, 90**
o-Chloronitrobenzene, **20, 45**
p-Chloronitrobenzene, **22, 32; 28, 14, 82**
 6-Chloro-8-nitroquinoline, **27, 52**
m-Chlorophenylmagnesium bromide, **28, 28**
m-CHLOROPHENYLMETHYLCARBINOL, **28, 28, 30, 32**
 Chlorophenylmethylcarbinols, **28, 28, 30**
 7-Chloro-4-quinolinol, **28, 39**
m-CHLOROSTYRENE, **28, 31**
 Chlorostyrenes, **28, 31, 33**
 CHOLESTENONE, **21, 18**
 Cholesterol, **21, 18**
 Chromium trioxide, **21, 6; 24, 39, 76**
 CINCHONIC ACID, 2-HYDROXY-, **28, 70**
 Cinnamic acid, **20, 77; 22, 26; 24, 21**
 CINNAMOYL CHLORIDE, **20, 77; 24, 21**
 Citral, bisulfite compound, **23, 78**
 purification of, **23, 78**
 Claisen condensation, with acetone and ethyl formate, **27, 92**
 with ethyl oxalate and ethyl succinate, **26, 42**
 with potassium ethoxide, **26, 42**
 with sodium amide, **28, 44**
 Claisen reaction, **20, 7, 32**
 Claisen rearrangement, **25, 49**
 Claisen's alkali, **25, 79**
 Clarke-Rahrs column, **24, 73**
 Clayton yellow paper, **22, 20, 22**
 Cleavage, of a disulfide, **20, 23**
 of a tetrahydrofuran ring, **25, 84**
 of 6-trityl group in 6-trityl- β -D-glucosetetraacetate, **22, 57**
 Clemmensen reduction, **20, 57**
 Clinton, **22, 2**
 Coconut oil, **20, 69**
 Condensation, of an acid and an amine, **20, 66**
 of an aldehyde and an acid, **20, 55**
 of an aldehyde and creatinine, **22, 90**
 of an aldehyde and malonic acid, **24, 92; 25, 51**
 of an aldehyde and malonic ester, **25, 42**
 of benzil with dibenzyl ketone, **23, 92**
 of citral and acetone, **23, 79**
 of an ester, **20, 26**
 of a ketone and an anhydride, **20, 6**
 of a ketone and cyanoacetic ester, **25, 46**
 of a ketone and an ester, **20, 7, 32; 28, 44**
 of a ketone and a hydroxy acid, **20, 62**
 of a nitroso compound and an amine, **25, 86**
 of a sodium sulfinate and *p*-nitrochlorobenzene, **22, 31**
 Condenser, partial, **20, 26**
 Congo red, **22, 20, 63, 66, 92, 93**
 Copper acetate, **20, 6; 21, 40, 47**
 COPPER ACETYLACETONE, **20, 6**
 Copper bronze, activation of, **20, 45**
 Copper chromite, **26, 83**
 Copper-chromium oxide, **22, 67**
 COPPER ETHYL DIACETYLACETATE, **21, 46**
 Copper helices, **20, 96**
 Copper oxide, **22, 67**
 Copper powder, **26, 50; 28, 50**
 Copper reaction vessel, **23, 102**
 Copper sulfate, **24, 23; 28, 25, 53**
 Cotton, absorbent, for drying, **20, 8, 9; 25, 1**
 Cottonseed oil, **22, 78, 85**
 use of hydrogenated, as oil bath, **24, 15**
 COUMARILIC ACID, **24, 33**
 Coumarin, **24, 33**

- Coumarin dibromide, **24, 33**
 COUMARIN, 4-METHYL-, **24, 69**
 Coupling, of allyl chloride, **27, 7**
 of aryl residues, **20, 45**
 Crab shells, **26, 36**
 Creatinine, **22, 90**
p-CRESOL, 2-BROMO-, **23, 11**
 Crotonaldehyde, **24, 92; 27, 66**
 Crotonic acid, **20, 101; 24, 98; 26, 55**
 Cupric acetate, **28, 45**
 Cupric carbonate, basic, **24, 64**
 Cupro-cupri sulfite, **28, 53**
 Cuprous bromide, **24, 22, 23**
 Cuprous chloride, **28, 46**
 Cuprous cyanide, **21, 89; 24, 14, 97; 28, 34**
 Curtius reaction, **24, 94**
 CYANAMIDE, METHYL-(1-NAPHTHYL-), **27, 56**
 Cyanoacetamide, **23, 60; 25, 63**
bis-(β -CYANOETHYL)-AMINE, **27, 3**
 Cyanogen bromide, **27, 56**
 Cyanohydrins, **20, 44; 22, 13, 16**
 ω -CYANOPELARGONIC ACID, **25, 96**
 9-CYANOPHENANTHRENE, **28, 7, 34**
 α -CYANO-*o*-TOLUIC ACID, **22, 30, 61**
 Cyclization, **20, 16, 26, 42, 73; 26, 29**
 acetoacetanilide to 4-methylcarbosty-
 ril, **24, 68**
 acet-*o*-toluidide to 2-methylindole, **22, 94**
 arylthiourea to aminobenzothiazole, **22, 17**
 3-carbethoxycoumarin synthesis, **28, 24**
 N-chloroamines to N-alkylpyrroli-
 dines, **25, 19**
 γ -chlorobutyronitrile to cyclopropyl
 cyanide, **24, 36**
 α -diketone and ketone to a cyclopen-
 tadienone, **23, 92**
 1,5-dimethyl-2-pyrrolidone synthesis,
27, 28
 2,3-diphenylindone synthesis, **27, 30**
 ethyl phenylacetylmalonate, **25, 74**
 indole synthesis, **23, 42**
 ketone phenylhydrazone to indole, **22, 98**
 malonic ester synthesis of cyclobutane
 acids, **23, 16**
 6-methoxy-8-nitroquinoline synthesis,
27, 48
 phenylanthranilic acid to chloroacri-
 dine, **22, 5**
 pyrazolone synthesis, **28, 87**
 quinoline synthesis, **28, 38, 49, 70**
 tartaric acid dinitrate to imidazole-
 4,5-dicarboxylic acid, **22, 66**
 CYCLOBUTANECARBOXYLIC ACID, **23, 18**
 1,1-CYCLOBUTANEDICARBOXYLIC ACID,
23, 16
- CYCLOHEXANEACETONITRILE, α -PHENYL-,
25, 25
cis-1,2-Cyclohexanediol, **28, 37**
trans-1,2-CYCLOHEXANEDIOL, **28, 35**
 1,3-CYCLOHEXANEDIONE, **27, 21**
 Cyclohexanone, **20, 42; 25, 22; 28, 8**
 CYCLOHEXANONE, 2-ALLYL-, **28, 8**
 Cyclohexene, **20, 28; 28, 35**
 2-CYCLOHEXEN-1-ONE, 4-CARBETHOXY-
 3,5-DIMETHYL-, **27, 24**
 2-CYCLOHEXEN-1-ONE, 3,5-DIMETHYL-,
27, 24
 Cyclohexyl bromide, **25, 26**
 α -CYCLOHEXYLPHENYLACETONITRILE,
25, 25
 CYCLOPENTADIENONE, TETRAPHENYL-,
23, 92
 CYCLOPROPANE, CYANO-, **23, 20; 24, 36**
 CYCLOPROPANECARBOXYLIC ACID, **24, 36**
 CYCLOPROPYL CYANIDE, **23, 20; 24, 36**
p-Cymene, **21, 96; 27, 86**
 CYSTEIC ACID MONOHYDRATE, **20, 23**
 Cystine, **20, 23**
- DDT, **26, 21**
 Deacetylation, **22, 34**
 Debromination, of hexabromostearic
 acid, **22, 83**
 of tetrabromostearic acid, **22, 77, 81**
 DECAMETHYLENE BROMIDE, **20, 24**
 DECAMETHYLENEDIAMINE, **27, 18**
 Decamethylene glycol, **20, 25**
 1,10-DECANEDIAMINE, **27, 18**
 DECANE, 1,10-DIBROMO-, **20, 24**
 Decarboxylation, **23, 18**
 of 1,3-dihydroxy-2-naphthoic acid, **25, 75**
 of imidazole-4,5-dicarboxylic acid, **22, 67**
 of an oximino acid to an oxime, **22, 27**
 Decomposition, diazonium salt to phenol,
23, 11; 25, 56
n-DECYL *p*-BROMOBENZENESULFONATE,
20, 51
n-Decyl mercaptan, **21, 38**
 Degradation, **20, 14**
 Dehydration, **20, 48, 74; 28, 31, 33**
 catalytic, **22, 39, 40**
 of an amide, **25, 61, 63, 69, 95**
 of 3,12-dihydroxy-*nor*-cholanlydi-
 phenylcarbinol, **24, 41**
 DEHYDROACETIC ACID, **20, 26; 21, 66**
 Dehydrogenation, by air and alkali, **22, 37**
 by bromine, **23, 94**
 by selenium, **27, 33**
 by sulfur, **24, 85**
 of a pyrroline to a pyrrole, **27, 33**
 Dehydrohalogenation, **26, 1; 27, 9, 77**
 Demethylation of a phenolic ether by
 hydriodic acid, **22, 91**

- Desiccator, vacuum, "dumb-bell" type, **23, 105**
 Desoxycholic acid, **24, 41, 42**
bisnor-Desoxycholic acid, **24, 40**
nor-Desoxycholic acid, **24, 38**
 Desulfonamidation, of 3,5-dibromosulfanilamide, **24, 49**
 of 3,5-dichlorosulfanilamide, **24, 48**
 Diacetalamine, **24, 5**
 3,12-Diacetoxy-*nor*-cholic acid, **24, 39**
 3,12-DIACETOXY-*bisnor*-CHOLANYLDIPHENYLETHYLENE, **24, 38, 41**
 4,4'-Diacetylaminodiphenylsulfone, **22, 34**
 2,7-Diacetylfluorene, **28, 5**
 DIACETYL METHANE, **20, 6**
 Diallylcyclohexanone, **28, 9**
 Diamines with carbon disulfide, **26, 35**
 4,4'-Diaminobiphenyl-3,3'-dicarboxylic acid, **27, 47**
 DIAMINOBIURET, **24, 58**
 4,4'-DIAMINODIPHENYLSULFONE, **22, 31**
 1,2-DIAMINO-4-NITROBENZENE, **21, 20**
o-Dianisidine, **21, 31**
 Diazoketone, **26, 14**
 1,3-DIAZOLE, **22, 65**
 DIAZOMETHANE, **26, 13**
 DIAZOMETHANE from N-nitroso- β -aminobutyl methyl ketone, **26, 28**
 drying of, **25, 31**
 Diazonium salt, reduction of, **21, 30**
 Diazotization, **20, 16, 73; 21, 31, 32, 34; 23, 11; 24, 22; 25, 56; 27, 81; 28, 52**
trans-DIBENZOYLETHYLENE, **20, 29**
 DIBENZOYLMETHANE, **20, 32**
 Dibenzyl ketone, **23, 92**
 α,α' -Dibromoadipic acid, debromination of, **26, 58**
 esterification of, **26, 58**
 2,6-DIBROMOANILINE, **24, 47**
m-Dibromobenzene, **24, 24**
 1,10-DIBROMODECANE, **20, 24**
 α,β -Dibromoglutaric acid, **26, 44**
 1,5-DIBROMOPENTANE, **23, 67**
 3,5-DIBROMOSULFANILAMIDE, **24, 48**
 Di-*n*-butylamine, **24, 44; 25, 14**
 Di-*n*-butylamine hydrobromide, **24, 45**
 Di-*n*-butylaminoethanol, **23, 24**
 β -Di-*n*-BUTYLAMINOETHYLAMINE, **23, 23**
 Di-*n*-butylaminoethyl bromide hydrobromide, **23, 23**
 γ -Di-*n*-BUTYLAMINOPROPYLAMINE, **24, 44**
 γ -Di-*n*-butylaminopropylamine dihydrochloride, **24, 45**
 Di- β -CARBETHOXYETHYLMETHYLAMINE, **20, 35**
 Di- β -CARBOMETHOXYETHYLMETHYLAMINE, **20, 37**
 α,α' -Dichloroacetamide, **20, 37**
 ω,ω' -Dichloroacetophenone, **23, 48**
 2,6-DICHLOROANILINE, **24, 47**
 Dichlorobenzaldehydes, **28, 30**
o-Dichlorobenzene, **20, 11**
 Di-(*p*-CHLOROPHENYL)-ACETIC ACID, **26, 21**
 1,1-Di-(*p*-chlorophenyl)-2,2-dichloroethylene, **26, 22**
 1,1-Di-(*p*-chlorophenyl)-ethylene, **26, 23**
 Di-(*p*-chlorophenyl)-methane, **26, 23**
 Dichlorophenylmethylcarbinols, **28, 30**
 1,1-Di-(*p*-chlorophenyl)-2,2,2-trichloroethane, **26, 21**
 4,7-DICHLOROQUINOLINE, **28, 38**
 Dichlorostyrenes, **28, 33**
 3,5-Dichlorosulfanilamide, **24, 47**
 α,α' -Dicyano-2,5-dihydroxy-*p*-benzene-diacetic acid, ethyl ester, **26, 25**
 α,α' -DICYANO- β -METHYLGLUTARAMIDE, **23, 60**
 Diels-Alder reaction, **22, 37; 23, 93**
 Diene synthesis, **22, 37, 40; 23, 93**
 Diethylamine, **27, 21**
 Diethylamine hydrochloride, **23, 31**
 DIETHYLAMINOACETONITRILE, **27, 20**
 DIETHYLAMINOETHYLAMINE, **23, 24**
 β -DIETHYLAMINOPROPIOPHENONE HYDROCHLORIDE, **23, 31**
 γ -Diethylaminopropylamine, **24, 46**
 DIETHYL BENZYL MALONATE, **21, 99**
 DIETHYL *sec*-BUTYLMALONATE, **21, 60**
 Diethyl α,δ -dibromoadipate, **26, 57**
 Diethylene glycol, **26, 21**
 Diethyl ketone, **22, 13; 25, 47**
 Diethyl malonate, **21, 60, 99; 25, 42**
 Diethyl- α -naphthylamine, **27, 57**
 Diethyl terephthalate, **26, 96**
 1,4-DIHYDRO-2,3-DIMETHYLANTHRAQUINONE, **22, 37**
 3,4-Dihydro-2-naphthoic acid, **26, 30**
 2,3-DIHYDROPYRAN, **23, 25; 27, 43**
 DIHYDRORESORCINOL, **27, 21**
 2,5-DIHYDROXYACETOPHENONE, **28, 42**
 2,6-DIHYDROXYACETOPHENONE, **21, 22**
 2,5-DIHYDROXY-*p*-BENZENEDIACETIC ACID, **26, 24**
 3,5-DIHYDROXYBENZOIC ACID, **21, 27**
 1,3-DIHYDROXY-2-NAPHTHOIC ACID, **25, 74**
 2,5-Dihydroxypropiophenone, **28, 43**
 Di-(γ -hydroxypropyl)-aniline, **26, 41**
 DIISOVALERYLMETHANE, **28, 44**
 DIKETENE, **21, 64**
 8,10-Diketotolulidine, **26, 41**
 1,3-Diketone, **20, 6, 32**
 α -Diketone synthesis, **23, 1**
 2,6-DIMETHOXYBENZONITRILE, **22, 35**
 3,3'-DIMETHOXYBIPHENYL, **21, 30**
 6,7-DIMETHOXY-3,4-DIHYDRO-2-NAPHTHOIC ACID, **26, 28**
 5,8-Dimethoxylepidine, **26, 47**
 6,7-Dimethoxy-2-naphthoic acid, **26, 30**

- β -(3,4-DIMETHOXYPHENYL)-ETHYL-AMINE, **23, 72**
 β , β -DIMETHYLACRYLIC ACID, **23, 27**
 Dimethylamine, **21, 84**
 Dimethylamine hydrochloride, **23, 30**
 β -DIMETHYLAMINOPROPIOPHENONE HYDROCHLORIDE, **23, 30**
 Dimethylaniline, **24, 19, 20, 21; 27, 62**
 3,4-DIMETHYLANILINE, **28, 46**
 2,3-DIMETHYLANTHRAQUINONE, **22, 37**
 3,3'-DIMETHYLBIPHENYL, **21, 30**
 2,3-DIMETHYLBUTADIENE-1,3, **22, 37, 39, 40**
 3,5-DIMETHYL-4-CARBETHOXY-2-CYCLOHEXENE-1-ONE, **27, 24**
 3,5-DIMETHYL-2-CYCLOHEXEN-1-ONE, **27, 24**
 2,2-Dimethylethylenimine, **27, 12**
 2,4-DIMETHYL-3-ETHYLPYRROLE, **21, 67**
 DIMETHYLETHYNYLCARBINOL, **20, 40; 22, 101**
 5,5-DIMETHYLHYDANTOIN, **20, 42**
 5,8-Dimethylepimine, **26, 47**
 6,8-Dimethylepimine, **26, 47**
 2,5-DIMETHYLMANDELIC ACID, **25, 33**
 Dimethyl- α -naphthylamine, **27, 56**
 2,7-Dimethyloctane, **28, 77**
 N,N-DIMETHYLPHENYLETHYLAMINE, **25, 89**
 1,2-Dimethylpyrrolidine, **25, 19**
 1,5-DIMETHYL-2-PYRROLIDONE, **27, 24**
 2,4-DIMETHYLQUINOLINE, **28, 49**
 2,4-DIMETHYLTHIAZOLE, **25, 35**
 sym.-Dimethylthiourea, **21, 84**
 Di-1-naphthylmethane, **24, 31**
 2,4-Dinitroaniline, **21, 21**
 m-Dinitrobenzene, **22, 35**
 2,5-DINITROBENZOIC ACID, **22, 44**
 3,4-DINITROBENZOIC ACID, **22, 47**
 3,5-DINITROBENZOIC ACID, **22, 48, 49**
 2,2'-DINITROBIPHENYL, **20, 45**
 1,4-DINITRONAPHTHALENE, **28, 52**
 Dinitronaphthalenes, **28, 52, 54**
 2,4-Dinitrophenol, **25, 5**
 2,5-Dinitrotoluene, **22, 46**
 Dioxane, **20, 72; 22, 36, 83; 23, 27**
 use of, in hydrogenations with Raney nickel, **21, 16**
 1,3-DIOXOLANE-4-METHANOL, 2,2-DIMETHYL-, **28, 73**
 DIPHENYLACETONITRILE, **28, 55**
 Diphenylacetyl chloride, **26, 14**
 DIPHENYLACETYLENE, **22, 50**
 1,4-DIPHENYL-1-BUTENE-1,4-DIONE, **20, 29**
 DIPHENYLDIAZOMETHANE, **24, 53**
 assay of, **24, 55**
 Di-(α -phenylethyl)-amine, **23, 70**
 Di-(β -phenylethyl)-amine, **23, 72**
 1,2-Diphenylethylene, **22, 50**
 Diphenylhydrazine, **20, 15**
 Diphenylhydrazine hydrochloride, **20, 15**
 2,3-DIPHENYLLINDONE (2,3-DIPHENYL-1-INDENONE), **27, 30**
 DIPHENYLIODONIUM IODATE, **22, 52**
 DIPHENYLIODONIUM IODIDE, **22, 52, 71**
 Diphenyliodonium salts, **22, 71**
 DIPHENYLKETENE, **20, 47**
 1,3-DIPHENYL-1,3-PROPANEDIONE, **20, 32**
 DIPHENYLPYRROLE, **27, 33**
 2,4-Diphenyl-2-pyrroline, **27, 33**
 Diphenyl selenide, **24, 91**
 DIPHENYLTHIOCARBAZIDE, **25, 38**
 DIPHENYLTHIOCARBAZONE, **25, 38**
 Di-*n*-PROPYLAMINOETHYLAMINE, **23, 24**
 γ -Di-*n*-propylaminopropylamine, **24, 46**
 Disproportionation, of diphenylthiocarbazine, **25, 38**
 of an iodoso and an iodoxy compound, **22, 52**
 of iodosobenzene by steam distillation, **22, 72**
 DITHIZONE, **25, 38**
 sym.-Diundecyl urea, **24, 95**
 Dodecanol, **20, 50**
n-Dodecyl alcohol, **20, 50**
n-Dodecyl bromide, **21, 36**
n-DODECYL *p*-BROMOBENZENESULFONATE, **20, 51**
n-DODECYL MERCAPTAN, **21, 36**
S-Dodecylthiuronium bromide, **21, 37**
n-DODECYL *p*-TOLUENESULFONATE, **20, 50**
 Dowtherm A, **28, 39, 40**
 Dry Ice, **20, 37, 41; 21, 64; 22, 101; 24, 3; 25, 25**
 cooling medium for condenser, **23, 20**
 use of, for internal cooling during nitration, **21, 96**
 Drying, use of absorbent cotton, **20, 8, 9; 25, 1**
 "Dumb-bell" vacuum desiccator, **23, 105**
 Durylacetonitrile, **25, 67**
 DYPNONE, **21, 39**
 Elimination, of hydrogen bromide from a dibromide, **22, 50; 25, 92**
 with rearrangement, **24, 33**
 of hydrogen bromide from a vinyl halide, **25, 93**
 Emulsin, **22, 53**
 ENANTHIC ACID, γ -HYDROXY-, LACTONE, **27, 68**
 ENANTHIC ANHYDRIDE, **26, 1**
 Enzymatic synthesis, **22, 53**
 1,5-EPOXYPENTANE, **23, 67, 90**
 1,5-EPOXYPENTENE-1, **23, 25**
 Esterification, **20, 4, 21, 24, 50, 77; 24, 18, 19, 20, 21; 25, 72**
 by azeotropic distillation with benzene, **22, 38**

Esterification—*Continued*

- by nitric acid, **22, 65**
- of desoxycholic acid, **24, 41**
- of lactic acid, **26, 4**
- of linoleic acid, **22, 77**
- of linolenic acid, **22, 83**
- of pyruvic acid with use of methyl ester column, **24, 72**
- Ester interchange, **26, 5, 19**
 - between polylactic acid and allyl alcohol, **26, 5**
- ETHANE, 1-BROMO-2-ETHOXY-, **23, 32**
- Ethanolamine, **26, 38**
- ETHANOL, 2-ISOPROPYLAMINO-, **26, 38**
- Ether, anhydrous, **22, 57**
- ETHER, BUTYL *o*-NITROPHENYL, **25, 9**
- β -Ethoxyethyl alcohol, **23, 32**
- β -ETHOXYETHYL BROMIDE, **23, 32, 33**
- β -ETHOXYETHYL CYANIDE, **23, 33**
- Ethoxymagnesiummalonic ester, **25, 73**
- 2-ETHOXY-1-NAPHTHALDEHYDE, **20, 11**
- 6-Ethoxy-8-nitroquinoline, **27, 52**
- β -ETHOXYPROPIONALDEHYDE ACETAL, **25, 1**
- β -ETHOXYPROPIONITRILE, **23, 33**
- Ethyl acetate, **20, 8; 23, 9**
 - dry, **20, 10**
- Ethyl acetoacetate, **20, 26; 21, 23, 46, 67; 23, 35; 24, 69; 27, 24, 35**
- Ethyl acrylate, **20, 36**
- Ethyl alcohol, anhydrous, **22, 59; 23, 9, 16, 24; 25, 45, 76**
- Ethyl alkylidenecyanoacetates, **25, 48**
- Ethyl-*n*-amylamine, **25, 19**
- ETHYL AZODICARBOXYLATE, **28, 58**
- ETHYL BENZALMALONATE, **25, 42**
- Ethyl benzoate, **20, 32; 23, 35, 98**
- ETHYL BENZOYLACETATE, **23, 35; 25, 7**
- Ethyl bromide, **22, 59**
 - as solvent, **23, 67**
- ETHYL BROMOACETATE, **21, 51; 23, 37**
- Ethyl α -bromoglutaconate, **26, 44**
- Ethyl α -bromoisobutyrate, **21, 53**
- ETHYL β -BROMOPROPIONATE, **20, 65**
- Ethyl-*n*-butylamine, **25, 19**
- ETHYL *n*-BUTYLCYANOACETATE, **26, 31**
- ETHYL CAPRYLATE, **20, 69**
- Ethyl α -carbethoxy- β -*m*-chloroanilinoacrylate, **28, 39**
- Ethyl carbonate, **23, 95, 97; 26, 33**
- Ethyl chloroacetate, **24, 82; 27, 71**
- Ethyl chlorocarbonate, **21, 81; 24, 60; 28, 58**
- Ethyl chlorocinnamate, **24, 83**
- Ethyl chloroformate, **21, 81; 24, 60; 28, 58**
- 2-ETHYLCHROMONE, **21, 42**
- Ethyl crotonate, **26, 54**
- Ethyl cyanoacetate, **25, 46; 26, 25, 31; 28, 87**

- ETHYL DIACETYLACETATE, **21, 46**
 - copper derivative, **21, 46**
- Ethyl (dialkylvinyl)-alkylcyanoacetates, **25, 46**
- ETHYL DIAZOACETATE, **24, 56**
- Ethyl diethoxymethylmalonate, **28, 61**
- ETHYL 1,3-DIHYDROXY-2-NAPHTHOATE, **25, 74**
- ETHYL 2,5-DIMETHYLPHENYLHYDROXYMALONATE, **25, 33**
- ETHYL α,α -DIMETHYL- β -PHENYL- β -HYDROXYPROPIONATE, **21, 53**
- Ethylene chloride, **20, 28; 22, 76; 25, 63**
- Ethylenediamine, **26, 34**
 - reaction with carbon bisulfide, **26, 34**
- ETHYLENEDIAMINE, *N,N*-DIBUTYL-, **23, 23**
- Ethylene oxide, **23, 85; 26, 39**
- ETHYLENE THIOUREA, **26, 34**
- Ethylenimine, 2,2-dimethyl, **27, 12**
 - hydrogenation of, **27, 13**
- ETHYL ETHOXYMETHYLENEMALONATE, **28, 39, 60**
- Ethyl ethylcyanoacetate, **26, 33**
- Ethyl ethylidene-*bis*-acetoacetate, **27, 24**
- ETHYL (1-ETHYLPROPENYL)-METHYLCYANOACETATE, **25, 44**
- ETHYL (1-ETHYLPROPYLDENE)-CYANOACETATE, **25, 46**
- Ethyl formate, **24, 12; 26, 29**
- ETHYL 1,16-HEXADECANEDICARBOXYLATE, **21, 48**
- ETHYL HYDRAZINECARBOXYLATE, **24, 58**
- Ethyl hydrazodicarboxylate, **28, 58**
- Ethyl hydrogen adipate, **25, 21**
- Ethyl hydrogen sebacate, **21, 48; 25, 21**
 - electrolysis of, **21, 48**
- ETHYL α -ISOPROPYLACETOACETATE, **27, 35**
- Ethyl isothiocyanate, **21, 82**
- Ethyl isovalerate, **28, 55**
- Ethyl 10-ketohendecanoate, **28, 79**
- Ethyl 6-ketoheptanoate, **28, 79**
- Ethyl 10-keto-16-methyloctadecanoate, **28, 79**
- Ethyl 10-keto-14-methyltetracosanoate, **28, 79**
- Ethyl 10-keto-13-methyltetradecanoate, **28, 79**
- Ethyl lactate, **21, 71**
- ETHYL LAURATE, **20, 69**
- ETHYL LINOLEATE, **22, 77**
- ETHYL LINOLENATE, **22, 83**
- Ethyl malonate, **23, 16; 28, 24, 60**
- Ethyl mercaptan, **22, 59**
- Ethyl *N*-methyl- β -aminopropionate, **20, 37**
- 1-Ethyl-2-methylpyrrolidine, **25, 19**
- ETHYL MYRISTATE, **20, 69**
- N*-Ethyl-1-naphthylcyanamide, **27, 56**

- 1-Ethyl-1-(1-naphthyl)-2-selenourea, **27, 59**
 Ethyl orthoformate, **25, 93, 28, 60, 84**
 Ethyl oxalate, **26, 42**
 ETHYL OXALYLSUCCINATE, **26, 42**
 Ethyl oxomalonate, **25, 33**
 ETHYL PENTANE-1,1,5,5 TETRACARBOXYLATE, **23, 18**
 Ethyl phenylacetylmalonate, **25, 73**
 ETHYL β PHENYL- β -HYDROXYPROPIONATE, **21, 51**
 Ethyl propionate, **21, 43**
 Ethyl propylcyanoacetate, **26, 33**
 4 ETHYLPYRIDINE, **27, 38**
 1-Ethylpyrrolidine, **25, 19**
 Ethyl succinate, **26, 42**
 Ethyl thiourea, **21, 84**
 S ETHYLTHIURONIUM BROMIDE, **22, 59**
 Ethyl *m*-tolylxanthate, **27, 82**
 ETHYL N-TRICARBOXYLATE, **24, 60**
 Ethyl γ -veratrylbutyrate, **26, 29**
 Ethynylcarbinols, **20, 40, 22, 101**
 1-ETHYNYLCYCLOHEXANOL 1, **20, 41**
 Extraction, continuous, **20, 99, 23, 49**
 hot, **20, 30**
 Extractor, continuous, **23, 49; 28, 66**
 shaking, **22, 78**
o EUGENOL, **25, 49**
 Fatty acids, from natural oils, **22, 75, 76, 79, 82**
 linseed, distilled, **22, 84**
 saturated, separation from unsaturated, **22, 76**
 unsaturated, **22, 75, 82**
 hexabromide test for, **22, 78**
 Fermentation, **22, 53**
 Ferric nitrate, **23, 20, 25, 25**
 Ferrous sulfate, **28, 11**
 Fieser's solution, **21, 110**
 Filter fabric, Pyrex glass, **22, 33, 65**
 Vinyon, **22, 33, 67**
 Filter paper, hardened, **22, 45**
 "Shark skin," **25, 97**
 Fischer indole synthesis, **22, 98**
 Flash distillation, **21, 85**
 Flask, modified Claisen, **22, 11**
 Fluorene, **28, 3**
 purification of, **28, 4**
 2 FLUORENECARBOXYLIC ACID, 9 OXO-, **28, 63**
 Fluorenone, **28, 92**
 purification of, **28, 92**
 FLUORENONE 2 CARBOXYLIC ACID, **28, 63**
 FLUORENONE, 2,4,7 TRINITRO-, **28, 91**
 Fluorescence of 9 aminoacridine hydrochloride, **22, 7**
m-Fluorostyrene, **28, 33**
 Formaldehyde, **20, 60, 24, 64**
 Formaldehyde solution, **27, 20, 41**
 Formalin, **22, 66, 25, 65, 89**
 Formanilide, **26, 41**
 Formhydrazide, **24, 13**
 Formic acid, **20, 66, 102, 23, 43, 25, 89, 26, 7, 11, 28, 35**
 FORMIC ACID, AZOBIS-, DIETHYL ESTER, **28, 58**
 FORMIC ACID, CHLORO-, BENZYL ESTER, **23, 13**
o Formotoluide, **23, 43**
 Formylaminoguanidine sulfate, **26, 11**
 Formylation by Claisen condensation, **26, 28**
 FORMYL *dl* METHYLTHREONINE, **20, 103, 104**
 Fractionating column, Fenske type, **25, 2**
 packed, **20, 96**
 Whitmore Lux type, **21, 14, 66, 24, 16**
 Friedel Crafts reactions, **20, 1, 29, 23, 102, 24, 26, 28, 1, 3, 26, 55**
 Fries rearrangement, **21, 25, 28, 42**
 Froth dissipation, **20, 3**
 Fructose, **24, 64, 66**
 FUMARYL CHLORIDE, **20, 29, 51**
 Fuming sulfuric acid, **27, 78**
 2 FURANACRYLIC ACID, **20, 55; 25, 51**
 FURAN, 2 (BROMOMETHYL) TETRAHYDRO-, **23, 88**
 2 FURANPROPIONIC ACID, TETRAHYDRO-, **27, 68**
 Furfural, **20, 55, 23, 70, 25, 51**
 FURFURYLAMINE, **23, 70**
 Furnace, construction of, **22, 40**
 hot tube, **23, 25**
 Furoic acid, **27, 60**
 FURYLACRYLIC ACID, **20, 55; 25, 51; 27, 68**
 Fusion, alkaline, of an aryl sulfonate, **21, 29**
 Fusion pot, **20, 86**
 Gas trap, **20, 1, 12, 29, 60, 77, 92, 106, 23, 48**
 Gattermann reaction, aldehyde synthesis, **23, 57**
 β GENTIOBIOSE OCTAACETATE, **22, 53**
 Glass helices, **20, 96**
d GLUCOSAMINE HYDROCHLORIDE, **26, 36**
 Glucose, **20, 75, 22, 1, 53**
 anhydrous, **20, 97**
 GLUCOSE OXIME, **20, 75**
 GLUCOSE PENTAACETATE, **22, 1**
 β *d* GLUCOSE-1,2,3,4,6 TETRAACETATE, **22, 56**
 β *d* GLUCOSE 2,3,4,6 TETRAACETATE, **25, 53**
 GLUTARIC ACID, β METHYL-, **23, 60**
 GLUTARIC ACID, α OXO-, **26, 42**
 Glyccol, **22, 75, 82, 27, 48, 28, 73**
 GLYCEROL, ISOPROPYLIDINE-, **28, 73**
 GLYCIDIC ACID, β METHYL β PHENYL-, 1-HYDROXY-, **24, 82**

- Glycine, **22**, **59**, **23**, **14**
ethyl ester hydrochloride, **24**, **56**
GLYCOCYAMINE, **22**, **59**
Glycolic acid, **24**, **63**
GLYCOINITRILE, **27**, **41**
Glycoside, hydrolysis of, **22**, **86**
Glyoxal, **24**, **63**
GLYOXAL BISULFITE, **24**, **61**
GLYOXALINE, **22**, **65**
GLYOXYLIC ACID, PHENYL-, **24**, **16**
Grignard reaction, *p* bromophenylselenophenol, **24**, **91**
 n butylselenol, **24**, **91**
 3,12 dihydroxy *nor* cholanyldiphenylcarbinol, **24**, **41**
 disoamylcadmium, **28**, **76**
 1-hydroxy-1-phenyl 1,2,3,4-tetrahydronaphthalene, **24**, **85**
 selenocresols, **24**, **91**
 selenophenol, **24**, **89**
 thiophenols, **24**, **91**
Guaiacol, **26**, **50**
GUAIACOL ALLYL ETHER, **25**, **49**
GUANIDINE, AMINO, BICARBONATE, **26**, **7**
GUANIDOACETIC ACID, **22**, **59**
- Haloform reaction, **23**, **27**
Helices, **20**, **96**
HEMIN, **21**, **53**
Hempseed oil, **22**, **85**
Heptabromostearic acid, **22**, **83**, **85**
Heptaldehyde, **23**, **70**
Heptane, **20**, **41**
Heptanoylchlororesorcinol, **20**, **58**
o HEPTANOYLPHENOL, **20**, **57**, **58**
p-HEPTANOYLPHENOL, **20**, **58**
Heptonic acid, **26**, **2**
HEPTOIC ANHYDRIDE, **26**, **1**
Heptoyl chloride, **26**, **2**
n HEPTYLAMINE, **23**, **70**
n-Heptyl mercaptan, **21**, **38**
o-*n*-HEPTYLPHENOL, **20**, **57**
Herschberg stirrer, **20**, **8**, **22**, **74**, **23**, **33**
HEXABROMOSTEARIC ACID, **22**, **82**
n-HEXADECYL *p* BROMOBENZENESULFONATE, **20**, **51**
n-HEXADECYL *p* FOLUENESULFONATE, **20**, **51**
1,5 HEXADILNE, **27**, **7**
HEXAHYDROPLUDOIONOL, **23**, **81**
HEXAMETHYLENE BROMIDE, **20**, **25**
HEXAMETHYLENE CHLOROHYDRIN, **28**, **65**
Hexamethylene dichloride, **28**, **66**
Hexamethylene glycol, **28**, **66**
HEXAMETHYLENE TRIAMINE, **22**, **66**
1 HEXANOI, 6 CHLORO, **28**, **65**
p *n* Hexoxy aniline, **25**, **10**
o-*n* Hexoxynitrobenzene, **25**, **10**
p *n* Hexoxynitrobenzene, **25**, **10**
n HEXYLAMINE, **23**, **72**
Hinsberg separation, **25**, **16**
- HOMOPHTHALIC ACID, **22**, **61**
HYDRATROPALDEHYDE, **24**, **87**
Hydrazine, anhydrous, **24**, **53**
 reaction of sulfate with methylsulfathiourea sulfate, **26**, **9**
Hydrazine hydrate, **20**, **48**, **21**, **68**, **70**, **24**, **12**, **53**, **58**, **28**, **58**
Hydrazine sulfate, **21**, **70**, **26**, **10**
Hydriodic acid, **22**, **91**
Hydrobromic acid, **20**, **82**, **102**, **103**, **22**, **39**
 48%, **23**, **67**; **24**, **22**
 recovery as constant-boiling acid, **23**, **68**
Hydrochloric acid, **23**, **86**, **28**, **66**
Hydrocinnamoyl chloride, **26**, **14**
Hydrocyanic acid, **22**, **25**
Hydrogen, electrolytic, **21**, **85**, **111**
Hydrogenation, apparatus for high-pressure, **21**, **108**
 dangers and precautions, **22**, **10**, **26**, **84**
 of a dinitrile, **27**, **18**
 of an ethylenimine, **27**, **13**
 of a ketimine, **27**, **28**
 of a nitrile, **27**, **33**
 of nitro compounds, **22**, **10**, **25**, **10**
 of resorcinol, **27**, **21**
 over palladium, **26**, **32**, **45**
 over platinum, **26**, **38**
Hydrogenation bomb, use of, as autoclave, **24**, **3**, **54**, **28**, **46**
Hydrogen bromide, **20**, **25**, **64**, **22**, **2**, **57**
 bromine free, **20**, **65**, **22**, **3**
Hydrogen chloride, **20**, **60**, **79**, **23**, **57**, **63**, **24**, **25**
 generator, **23**, **58**
Hydrogen cyanide, addition to ethyl crotonate, **26**, **54**
Hydrogenolysis, of 2 chlorolepidine, **26**, **45**
 of tetrahydrofurfuryl alcohol to 1,5 pentandiol, **26**, **83**
 of various chlorolepidines, **26**, **47**
Hydrogen peroxide, **20**, **70**, **23**, **66**, **24**, **47**, **48**, **49**, **50**, **26**, **90**, **28**, **14**, **35**
Hydrogen sulfide, **20**, **15**, **21**, **22**, **14**, **23**, **7**, **24**, **65**, **85**, **27**, **58**, **28**, **16**
Hydrolysis, **20**, **82**, **92**, **98**, **25**, **33**, **74**, **27**, **1**
 and decarboxylation of a β keto ester, **26**, **43**
 of an acetal, **25**, **93**
 of an acetamino compound, **22**, **32**, **25**, **79**
 of an amide to an acid, **22**, **14**, **23**, **61**
 of chitin, **26**, **36**
 of a creatinine derivative to an amino acid, **22**, **91**
 of a glucosidic bromide, **25**, **53**
 of an isonitroso ketone to an α diketone, **28**, **1**

Hydrolysis—*Continued*

- of a ketimine, **28, 7**
- of a methylglycoside, **22, 86**
- of a nitrile to an acid, **22, 23, 61; 24, 16, 36, 96; 25, 66; 26, 55**
- of a nitrile to an amide, **22, 13**
- of an oxime, **27, 16**
- of a substituted cyanomalonate ester, **26, 25**
- Hydroquinone, **20, 64; 28, 68**
 - as an inhibitor, **22, 39, 41; 28, 94, 96**
- Hydroquinone diacetate, **28, 68, 42**
- Hydroquinone dipropionate, **28, 43**
- o*-Hydroxyacetophenone, **21, 43, 45**
- m*-Hydroxybenzaldehyde, **25, 55**
- ω -Hydroxycaproic acid, **27, 70**
- 2-Hydroxycinchoninic acid, **28, 70**
- Hydroxylamine, **20, 74; 28, 80**
- Hydroxylamine hydrochloride, **20, 74; 22, 26; 28, 80**
- β -Hydroxylaminocinnamic acid, **22, 26**
- 2-Hydroxy-3-methoxybenzaldehyde, oxidation with hydrogen peroxide, **26, 90**
- 4(5)-Hydroxymethylimidazole hydrochloride, **24, 64**
- Hydroxymethylimidazole picrate, **24, 64**
- 2-Hydroxy-1-naphthaldehyde, **22, 63**
- 3-Hydroxy-2-naphthoic acid, **22, 19**
- 2-Hydroxy-1,4-naphthoquinone, **21, 56**
- 2-Hydroxy-5-nitrobenzyl chloride, **20, 59**
- 5-Hydroxypentanal, **27, 43**
- α -Hydroxyphenazine, methylation to quaternary salt, **26, 87**
- 2-(β -Hydroxypropyl)-pyridine, **23, 83**
- 2-(γ -Hydroxypropyl)-pyridine, **23, 85**
- N-(γ -Hydroxypropyl)-tetrahydroquinoline, **26, 41**
- Hypophosphorous acid, **21, 30**
- Imidazole, **22, 65**
- Imidazole-4,5-dicarboxylic acid, **22, 66**
- 4-Imidazolemethanol hydrochloride, **24, 64**
- 2-Imidazolidinethione, **26, 34**
- 2-Imino-1-ethylnaphtho[1,2]selenazoline, **27, 55**
- 2-Imino-1-methylnaphtho[1,2]selenazoline, **27, 55**
- Indazole, **20, 74**
- Indole, **23, 42**
- Indole, 2-methyl, **22, 94**
- Indole, 2-phenyl, **22, 98**
- Indone, 2,3-diphenyl-, **27, 30**
- Inhibitor, **20, 36, 48, 65; 22, 39, 41**
- Iodination of phthalic anhydride, **27, 78**
- Iodine, **27, 78; 28, 16, 22, 49**
- Iodine value, **22, 79, 84**

- Iodobenzene, **22, 69, 71, 72, 73**
- Iodobenzene dichloride, **22, 69, 70, 73**
- p*-Iodobenzyl alcohol, **24, 81**
- p*-Iodobenzyl bromide, **24, 81**
- Iodonium compound, **22, 52**
- Iodoso and iodoxy compounds, differentiation, **22, 71**
- Iodosobenzene, **22, 52, 70, 72**
- Iodotoluene dichlorides, *o*-, *m*-, *p*-, **22, 70**
- Iodoxybenzene, **22, 52, 72, 73**
- Iron powder as reducing agent, **22, 12**
- Irradiation, **20, 81, 92, 101**
- Isatin, **28, 70**
- Isatoic anhydride, **27, 45**
- Isoamyl bromide, **28, 76**
- Isoamylmagnesium bromide, **28, 76**
- Isobutyl alcohol, **23, 43**
- Isobutyramide, **25, 58**
- Isobutyronitrile, **25, 61**
- Isobutyryl chloride, **24, 20; 25, 58**
- Isocaproic acid, **21, 74**
- Isocaproic acid, α -amino, **21, 74**
- Isodurylacetonitrile, **25, 67**
- β -Isodurylaldehyde, **21, 110; 23, 57, 59**
- β -Isoduryllyl chloride, **21, 77**
- dl*-Isoleucine, **21, 60**
- Isonitrosopropiophenone, **23, 1**
- p*-Isopropoxyaniline, **25, 10**
- p*-Isopropoxynitrobenzene, **25, 10**
- Isopropyl alcohol, **24, 26; 27, 35**
- Isopropylamine, **26, 39**
- 2-Isopropylaminoethanol, **26, 38**
- Isopropyl ether, recrystallization from, **22, 2**
 - removal of peroxides from, **22, 3**
- dl*-Isopropylideneglycerol, **28, 73**
- Isopropyl nitrite, **24, 26**
- Isovaleric acid, α -acetyl, ethyl ester, **27, 35**
- Isovaleric acid, dry, **20, 106**
- Isovaleric acid monohydrate, **20, 106**
- Isovaleryl chloride, **24, 21**
- Julolidine, **26, 40**
- Kerosene, purified, **24, 7**
- Ketene, **21, 13, 64**
- Ketene diethylacetal, **23, 45**
- Ketene, diethyl ketal, **23, 45**
- Ketene dimer, **21, 4, 64**
- "Ketene lamp," **21, 65**
- Keto acid, **20, 2**
- α -Ketoglutaric acid, **26, 42**
- Ketone, 2-fluorenyl methyl, **28, 3, 63**
- Ketone, methyl 9-phenanthryl, **28, 6**
- Ketone, methyl 2-thienyl, **28, 1**
- Knoevenagel condensation, **23, 60; 24, 92; 25, 42, 51; 27, 24; 28, 24**
- Kolbe synthesis of an alkyl α,ω -dicarboxylate, **21, 48**

- KRYPTOPYRROLE**, **21**, **67**
- LACTAMIDE**, **21**, **71**
- Lactic acid, alkyl esters, **26**, **6**
 esterification of, **26**, **4**
 methyl ester, **26**, **6**
 polymer of, **26**, **5**
- LACTIC ACID, ALLYL ESTER**, **26**, **4**, **5**
- Laurel wax, **20**, **68**
- Lauroylacetone, **28**, **46**
- Lauroyl chloride, **24**, **94**
- Lauryl alcohol, **20**, **50**
- LAURYL MERCAPTAN**, **21**, **36**
- S-LAURYLTHIURONIUM BROMIDE**, **21**, **37**
- LAURYL *p*-TOLUENESULFONATE**, **20**, **50**
- Lead acetate, **24**, **62**
- Lead dioxide, **21**, **1**
- Lead hydroxide, **22**, **15**
- Lead tetraacetate, **21**, **1**, **3**
- LEPIDINE**, **26**, **45**
 various methods of preparation, **26**, **48**
- LEPIDINE, 2-CHLORO-**, **24**, **28**; **26**, **45**
- dl*-LEUCINE**, **21**, **74**
- Levulinic acid, **27**, **28**
- LINOLEIC ACID**, **22**, **75**
TETRABROMIDE, **22**, **76**
- LINOLENIC ACID**, **22**, **82**
HEXABROMIDE, **22**, **82**, **85**
- LINOLIC ACID**, **22**, **75**
- Linseed oil, **22**, **82**, **84**, **85**
- Liquid ammonia, **27**, **18**
- Lithium**, **23**, **83**
 cutting, **23**, **84**
 sand, **23**, **84**
- Magnesium**, **21**, **46**, **77**, **79**; **24**, **41**, **85**,
90; **27**, **30**, **65**; **28**, **6**, **28**, **76**, **84**
 in malonic ester synthesis, **25**, **73**
- Magnesium powder**, **20**, **21**
- Magnesium turnings**, **27**, **7**
- Maleic anhydride**, **20**, **51**; **23**, **93**
- Malonic acid**, **24**, **92**
 drying of, **25**, **52**
 substituted, **21**, **61**
 bromination of, **21**, **61**, **100**
 decarboxylation of, **21**, **61**, **101**; **25**,
33, **51**
- MALONIC ACID, BENZAL-, DIETHYL**
ESTER, **25**, **42**
- MALONIC ACID, ETHOXYMETHYLENE-, DI-**
ETHYL ESTER, **28**, **39**, **60**
- MALONONITRILE**, **25**, **63**
- MANDELAMIDE**, **20**, **62**
- MANDELIC ACID**, **20**, **62**; **23**, **48**
- MANDELIC ACID, 2,5-DIMETHYL-**, **25**, **33**
- Mannich reaction**, **23**, **30**
- d*-MANNOSE**, **22**, **86**
- Manometer**, **25**, **15**, **22**
- l*-Menthol**, **23**, **52**
- l*-MENTHOXYACETIC ACID**, **23**, **52**, **55**
- l*-MENTHOXYACETYL CHLORIDE**, **23**, **55**
- Mercuric acetate**, **20**, **81**, **101**
- Mercuric chloride**, **20**, **57**; **21**, **8**; **23**, **86**
- Mercuric oxide**, **20**, **47**, **103**
 yellow, **24**, **54**
- Mercury**, **22**, **91**, **92**
- Mercury valve**, **25**, **15**, **22**
- MESITALDEHYDE**, **21**, **110**; **23**, **57**, **59**
- MESITOIC ACID**, **21**, **78**
- MESITOYL CHLORIDE**, **21**, **77**, **110**
- MESITYLACETIC ACID**, **25**, **65**
- MESITYLACETONITRILE**, **25**, **66**
- Mesitylene**, **23**, **57**; **25**, **65**
- Metalation of α -picoline by phenyl**
lithium, **23**, **84**
- Metal bath**, **20**, **48**
 adhering to glass, prevention of, **22**,
95
- Metal reaction vessel**, **23**, **102**
- β -Methallyl lactate**, **26**, **6**
- METHANE, CHLOROTRIPHENYL-**, **23**, **100**,
102
- METHANE, DIAZO-**, **25**, **28**
- METHANE, DIAZODIPHENYL-**, **24**, **53**
- Methoxyacetoneitrile**, **21**, **79**
- ω -METHOXYACETOPHENONE**, **21**, **79**
- 3-Methoxy-1,2-benzoquinone, condensa-**
tion with *o*-phenylenediamine, **26**,
87
- 6-Methoxy-5-bromo-8-nitroquinoline**,
27, **52**
- 7-Methoxy-3,4-dihydro-2-naphthoic**
acid, **26**, **30**
- 2-METHOXYDIPHENYL ETHER**, **26**, **50**
- 5-(3-METHOXY-4-HYDROXYBENZAL)-**
CREATININE, **22**, **90**, **93**
- 5-(3-METHOXY-4-HYDROXYBENZYL)-**
CREATININE, **22**, **90**
- 6-Methoxylepidine**, **26**, **48**
- 6-Methoxylepidine monohydrate**, **26**, **47**
- 2-Methoxy-4'-methylidiphenyl ether**, **26**,
51
- 2-Methoxy-5-methyldiphenyl ether**, **26**,
51
- 2-METHOXY-1,4-NAPHTHOQUINONE**, **21**,
57
- 8-Methoxy-6-nitroquinoline**, **27**, **52**
- 6-METHOXY-8-NITROQUINOLINE**, **27**, **48**
- 6-Methoxy-8-nitroquinoline sulfate**, **27**,
52
- α -METHOXYPHENAZINE**, **26**, **86**
- α -Methoxyphenazine, demethylation of**,
26, **87**
- METHYL β -(1-ACENAPHTHOYL)-PROPIO-**
NATE, **20**, **4**
- Methyl acetoacetate**, **24**, **70**
- p*-Methylacetophenone, oxidation of**,
26, **95**
- 4-METHYL-7-ACETOXYCOUMARIN**, **21**, **24**
- Methyl acrylate**, **20**, **64**, **81**; **26**, **19**
- METHYLAL**, **20**, **60**
- Methylamine**, **20**, **36**; **27**, **28**

Methylamine—*Continued*

anhydrous, **20**, **35**
 30% aqueous solution, **25**, **28**
 35% aqueous solution, **21**, **81**
 generator, **20**, **35**
 hydrochloride, **21**, **82**
 N-Methylaminoaromatic acids, **22**, **93**
 Methyl-*n*-amylamine, **25**, **19**
 Methyl amyl ketone, **23**, **70**
 Methylaniline, **20**, **11**, **66**; **26**, **41**
 Methylation, **20**, **97**; **25**, **44**, **91**
 METHYL α -BROMO- β -METHOXYPROPIONATE, **20**, **81**
 METHYL β -BROMOPROPIONATE, **20**, **64**
 METHYL 5-BROMOVALERATE, **26**, **52**
 Methyl-*n*-butylamine, **25**, **19**
 1-Methyl-2-*n*-butylpyrrolidine, **25**, **19**
 Methyl carbitol, **22**, **32**
 4-METHYLCARBOSTYRIL, **24**, **28**, **68**
 Methyl chloride, **27**, **65**
 4-METHYLCOUMARIN, **24**, **69**
 METHYL ω -CYANOPELARGONATE, **25**, **69**
 Methylcyclohexane, **21**, **16**
 Methyl desoxycholate, **24**, **41**
 Methyl α,β -dibromopropionate, **20**, **82**
 N-METHYL-3,4-DIHYDROXYPHENYL-ALANINE, **22**, **89**, **91**, **93**
 β -(3,4-METHYLENEDI-OXYPHENYL)-ETHYLAMINE, **22**, **72**
 Methyl ester column, **24**, **72**, **73**
 METHYLETHYLETHYNYLCARBINOL, **20**, **41**; **22**, **101**
 5-METHYL-5-ETHYLHYDANTOIN, **20**, **44**
 Methyl ethyl ketone, **20**, **41**
 Methyl ethyl ketone cyanohydrin, **20**, **44**
 N-METHYLFORMANILIDE, **20**, **11**, **66**
o-METHYLFORMANILIDE, **23**, **43**
 Methyl β -formylpropionate, **21**, **88**
 α -Methylglucoside, **20**, **99**
 β -METHYLGUTARIC ACID, **23**, **60**
 Methyl hydrogen adipate, **26**, **52**
 METHYL HYDROGEN SUCCINATE, **25**, **19**
 4-METHYL-7-HYDROXY-8-ACETYLCOUMARIN, **21**, **25**
 4-METHYL-7-HYDROXYCOUMARIN, **21**, **23**
 1-METHYL-2-IMINO- β -NAPHTHOTHIAZOLINE, **27**, **53**
 2-METHYLINDOLE, **22**, **94**
 Methyl iodide, **28**, **6**
 Methyl isobutyl ketone, **28**, **45**
 METHYL ISOTHIOCYANATE, **21**, **81**, **83**
 Methyl isothiouraea, reaction of sulfate with hydrazine sulfate, **26**, **9**
 Methyl 4-keto-5-methyloctanoate, **28**, **79**
 METHYL 4-KETO-7-METHYLOCTANOATE, **28**, **75**
 Methyl lactate, **26**, **6**
 6-Methyllepidine, **26**, **47**
 8-Methyllepidine, **26**, **47**

Methylmagnesium iodide, **28**, **6**, **30**, **33**
 α -Methyl-*d*-mannoside, **22**, **86**
 Methyl mercaptan, **26**, **9**
 N-METHYL-(3-METHOXY-4-HYDROXY-PHENYL)-ALANINE, **22**, **91**
 2-Methyl-6-methoxyquinoline, **26**, **47**
 METHYL MYRISTATE, **20**, **67**
 α -Methylnaphthalene, **26**, **93**
 N-METHYL-1-NAPHTHYLCYANAMIDE, **27**, **56**, **58**
 1-Methyl-1-(1-naphthyl)-2-selenourea, **27**, **59**
 1-METHYL-1-(1-NAPHTHYL)-2-THIO-UREA, **27**, **53**, **58**
 Methyl-*n*-octylamine, **25**, **19**
 Methyl oleate, **27**, **76**
 METHYL PALMITATE, **20**, **67**
 METHYLPHENYLDIKETONE, **23**, **1**
 β -(2-METHYLPHENYL)-ETHYLAMINE, **23**, **72**
 β -(3-METHYLPHENYL)-ETHYLAMINE, **23**, **72**
 β -(4-METHYLPHENYL)-ETHYLAMINE, **23**, **72**
m-Methylphenylmethylcarbinol, **28**, **30**
 N-Methyl-2-pyridone, **26**, **18**
 1-Methylpyrrolidine, **25**, **19**
 METHYL PYRUVATE, **24**, **72**
 METHYL SEBACAMATE, **25**, **71**
 METHYLSUCCINIC ACID, **26**, **54**
 various methods for preparation of, **26**, **56**
 Methyl sulfate, **20**, **97**
 antidote, **20**, **97**
 α -Methyltetrahydrofuran, **26**, **83**
 METHYLTHIOUREA, **21**, **83**
 Mineral oil, **23**, **103**
 Monel-metal stirrer, **20**, **99**
 Monoalkylcyanoacetates, **26**, **33**
 Monochloroacetic acid, **28**, **94**
 MONOPERPHTHALIC ACID, **20**, **70**
 MUCOBROMIC ACID, **27**, **60**
 MUONIC ACID, **26**, **57**
 various methods of preparation, **26**, **60**
 MYRISTIC ACID, **20**, **69**
 Myrtle wax, **20**, **68**
 β -NAPHTHALDEHYDE, **21**, **84**; **23**, **63**
 2-NAPHTHALDEHYDE, **21**, **84**; **23**, **63**
 1-NAPHTHALDEHYDE, 2-HYDROXY-, **22**, **63**
 β -Naphthaldehydimine-stannichloride, **23**, **63**
 Naphthalene, **24**, **30**
 NAPHTHALENE, 1,4-DINITRO-, **28**, **52**
 1,3-NAPHTHALENEDIOL, **25**, **73**
 1,(2)-NAPHTHALENONE, 3,4-DIHYDRO-, **20**, **94**
 Naphthalic anhydride, **24**, **1**, **2**
 β -Naphthoic acid, **21**, **86**

- 2-NAPHTHOIC ACID, 3-AMINO-, **22, 19**
 3,4-DIHYDRO-6,7-DIMETHOXY-, **26, 28**
 β -Naphthol, **20, 18; 22, 23, 63**
 1-NAPHTHONITRILE, **21, 89**
 2-Naphthonitrile, **23, 63**
 1,4-Naphthoquinone, **22, 37**
 1,2-Naphthoquinone-4-sulfonate, ammonium, **21, 56**
 1,2-NAPHTHOQUINONE-4-SULFONATE, AMMONIUM AND POTASSIUM, **21, 91**
 NAPHTHORESORCINOL, **25, 73**
 β -NAPHTHOYL CHLORIDE, **21, 85**
 β -Naphthylamine, **22, 23**
 1-NAPHTHYLAMINE, 4-NITRO-, **28, 80**
 β -Naphthyl ethyl ether, **20, 11**
 α -Naphthyltrimethylammonium bromide, **27, 57**
 Nef reaction, **20, 40**
 Nichrome helices, **20, 96**
 Nickel-aluminum alloy, **21, 15, 16; 27, 68**
 Nickel catalysts, Raney, **21, 15; 22, 9, 12; 23, 68, 71, 81, 90; 25, 10; 27, 13, 18, 22, 28, 33**
 Universal Oil Products, **27, 22**
 Nitrate ester preparation, **22, 65**
 Nitrating mixture, **27, 62; 28, 91**
 Nitration in acetic acid, **25, 78**
 Nitric acid, **27, 84, 86**
 anhydrous, **21, 105, 106**
 fuming, **22, 48, 65; 23, 3; 28, 91**
 Nitrile formation, **20, 74; 21, 89; 25, 61, 63, 66, 69, 95; 28, 34**
 4-NITRO-4'-ACETANINODIPHENYLSULFONE, **22, 32**
 3-Nitro-4-aminoanisole, **27, 48**
 3-Nitro-4-aminotoluene, **22, 47**
 p -Nitroaniline, **26, 61**
 o -NITROBENZALDEHYDE, **24, 75; 28, 11**
 m -Nitrobenzaldehyde, **25, 55**
 o -Nitrobenzaldiacetate, **24, 75**
 Nitrobenzene, **20, 1; 22, 28; 24, 70; 25, 80**
 p -Nitrobenzenediazonium borofluoride, **26, 61, 62**
 p -Nitrobenzoic acid, **23, 66**
 m -Nitrobenzoyl chloride, **23, 66**
 p -Nitrobenzoyl chloride, **23, 65**
 m -NITROBENZOYL PEROXIDE, **23, 66**
 p -NITROBENZOYL PEROXIDE, **23, 65**
 p -NITROBENZYL ACETATE, **24, 79, 81**
 p -NITROBENZYL ALCOHOL, **24, 81**
 p -Nitrobenzyl chloride, **24, 79**
 p -Nitrochlorobenzene, **22, 32**
 2-NITRO- p -CYMENE, **21, 96; 22, 9**
 m -NITRODIMETHYLANILINE, **27, 62**
 p -Nitrodimethylaniline, **27, 63**
 Nitrogen atmosphere, **22, 94; 23, 42, 83**
 Nitrogen peroxide, **25, 34**
 Nitroguanidine, reduction of, **26, 7**
 5-NITROINDAZOLE, **20, 73**
 2-NITRO 4 METHOXYACETANILIDE, **25, 78**
 2-NITRO-4-METHOXYANILINE, **25, 78**
- 2-NITRO-6-METHOXYBENZONITRILE, **22, 35**
 α -Nitronaphthalene, **28, 80**
 4-Nitronaphthalene-1-diazonium sulfate, **28, 52**
 4-NITRO-1-NAPHTHYLAMINE, **28, 52, 80**
 3-NITRO-4-NITROSOTOLUENE, **22, 47**
 o -Nitrophenol, **25, 9**
 p -Nitrophenol, **20, 60**
 p -NITROPHENYLARSONIC ACID, **26, 60**
 various methods of preparation, **26, 62**
 p -NITROPHENYL SULFIDE, **28, 82**
 Nitrosation, of β -methylaminoisobutyl methyl ketone, **25, 28**
 of phenacyl chloride, **24, 25**
 NITROSOBENZENE, **25, 80**
 N-NITROSO- β -METHYLAMINOISOBUTYL METHYL KETONE, **25, 28**
 Nitrosomethylurethan, **26, 13**
 2-NITROSO-5-NITROTOLUENE, **22, 44**
 Nitrosylsulfuric acid, **28, 52**
 o -Nitrotoluene, **24, 76**
 p -Nitrotoluene, **21, 97**
 Nitrous acid, **22, 96**
 NONAMETHYLENE BROMIDE, **20, 25**
 4,6-NONANEDIONE, 2,8-DIMETHYL-, **28, 44**
 n -Nonyl mercaptan, **21, 38**
- OCTADECANEDIOIC ACID, DIETHYL ESTER, **21, 48**
 n -OCTADECYL p -BROMOBENZENESULFONATE, **20, 51**
 n -Octadecyl mercaptan, **21, 38**
 n -OCTADECYL p -TOLUENESULFONATE, **20, 51**
 Octanoylchlororesorcinol, **20, 59**
 o -Octanoylphenol, **20, 58**
 p -Octanoylphenol, **20, 58**
 Octanoylresorcinol, **20, 58**
 n -Octyl mercaptan, **21, 38**
 Oxidation, by air, **20, 94**
 by air and alkali, **22, 37**
 by bromine water, **20, 23**
 by chlorine water, **28, 59**
 by fuming nitric acid, **23, 3**
 by hydrogen peroxide, **20, 70; 28, 14, 35**
 in formic acid, **28, 35**
 by iodine, **28, 16**
 by nitric acid, **27, 84**
 by potassium chlorate, **23, 6**
 by potassium permanganate, **20, 79**
 by sodium dichromate and acetic acid, **28, 63**
 by sodium dichromate and sulfuric acid, **25, 81**
 conversion of acetyl to carboxyl group, **26, 95; 28, 63**
 of an aldehyde by selenious acid, **24, 61**

Oxidation—*Continued*

- of an amine to a nitroso compound, **22, 44, 47**
- of *p*-cymene, **27, 86**
- of a hydrazine derivative, **28, 59**
- of a hydrocarbon to a quinone, **24, 1**
- of a hydroxylamine to a nitroso compound, **25, 81**
- of iodobenzenedichloride to iodoxybenzene, **22, 73**
- of a methyl group to a carboxyl group, **22, 45, 47**
- of a nitroso compound to a nitro compound, **22, 45, 47**
- of *o*-nitrotoluene to *o*-nitrobenzaldehyde, **24, 75**
- of an olefin to an acid, **24, 39**
- of a thioacid to an acyl disulfide, **28, 16**
- of a thiophenol to a disulfide, **28, 14**
- of *o*-xylene, **27, 84**
- with bromine of a silver salt, **26, 53**
- Oxides of nitrogen, **23, 3**
- Oximation, **20, 75**
- OZONE, **26, 63**
 - absorption of, **26, 67**
 - analysis for, **26, 68**
 - destruction of, **26, 68**
 - various methods for preparation, **26, 76**
- Ozonization of organic compounds, **26, 71**
- OZONIZER, FOR THE LABORATORY, **26, 63**
 - of Pyrex glass, **26, 76**
- PALLADIUM, ON BARIUM CARBONATE, **26, 77**
 - ON BARIUM SULFATE, **26, 77**
 - ON CARBON, **26, 31, 45, 78**
 - recovery from spent catalyst, **26, 80**
- PALLADIUM CATALYSTS, **26, 77**
 - by reduction with formaldehyde or hydrogen, **26, 79**
 - various methods of preparation, **26, 32, 46, 81**
- PALLADIUM CHLORIDE ON CARBON, **26, 78**
- PALMITIC ACID, **20, 69**
- Paraffin, **23, 103**
- Paraformaldehyde, **23, 30; 24, 30**
- Paraldehyde, **24, 61**
- PELAGONIC ACID, 8-CYANO-, METHYL ESTER, **25, 69**
- o*-Pelargonylphenol, **20, 58**
- p*-Pelargonylphenol, **20, 58**
- PENTAACETYL-*d*-GLUCONONITRILE, **20, 14, 74**
- PENTAMETHYLENE BROMIDE, **23, 67**
- PENTAMETHYLENE GLYCOL, **26, 83**
- PENTAMETHYLENE OXIDE, **22, 67, 90**
- 1,5-PENTANDIOL, **26, 83, 85**
- PENTANE, 1,5-DIBROMO-, **23, 67**

- 2,4-PENTANEDIONE, **20, 6**
- 2-PENTENOIC ACID, 2-CYANO-3-ETHYL-, ETHYL ESTER, **25, 46**
- 3-PENTENOIC ACID, 2-CYANO-3-ETHYL-2-METHYL-, ETHYL ESTER, **25, 44**
- 4-PENTEN-1-OL, **25, 84**
- Pentose synthesis, **20, 14**
- Peracid, **20, 70; 22, 44**
- Perkin reaction, **20, 55**
- PEROXIDE, BIS(*p*-NITROBENZOYL-), **22, 65**
- Peroxides, removal from isopropyl ether, **22, 3**
 - removal from α -tetralone, **20, 95**
- PERPHTHALIC ACID, MONO-, **20, 70**
- Petroleum ether, **23, 102, 104**
- Phenacyl chloride, **24, 25, 26**
- Phenanthrene, **28, 19**
 - purification of, **28, 19**
- PHENANTHRENE-9-ALDEHYDE, **28, 83**
- PHENANTHRENE, 9-BROMO-, **28, 19**
- 9-PHENANTHRENECARBONITRILE, **28, 7, 34**
- 9-PHENANTHRENECARBOXYALDEHYDE, **28, 83**
- 9-Phenanthrylmagnesium bromide, **28, 83**
- PHENETHYLAMINE, **23, 71**
- Phenol, **20, 77; 22, 6; 24, 69**
- PHENOL, 2-AMINO-4-NITRO-, **25, 5**
- Phenol red, **22, 91**
- 9-Phenoxyacridine, **22, 7**
- Phenylacetyl chloride, **26, 14**
- dl*-PHENYLALANINE, **21, 99**
- α -Phenyl- α -aminobutyric acid, methylation of, **25, 91**
- 1-PHENYL-3-AMINO-5-PYRAZOLONE, **28, 87**
- N-Phenylanthranilic acid, **22, 5**
- PHENYL AZIDE, **22, 96**
- p*-PHENYLAZOBENZOIC ACID, **25, 86**
- p*-PHENYLAZOBENZOYL CHLORIDE, **25, 87**
- Phenylbenzoyldiazomethane, **20, 48**
- α -Phenyl- β -benzoylpropionitrile, **27, 33**
- PHENYL CINNAMATE, **20, 77**
- 1-Phenyldialin, **24, 84**
- β -PHENYLDITHIOCARBAZIC ACID, PHENYLDYDRAZINE SALT, **25, 38**
- o*-Phenylenediamine, **20, 16**
- α -PHENYLETHYLAMINE, **23, 68**
- β -PHENYLETHYLAMINE, **23, 71; 25, 89**
- PHENYLETHYLAMINE, *N,N*-DIMETHYL-, **25, 89**
- β -PHENYLETHYLDIMETHYLAMINE, **25, 89**
- dl*-PHENYLGLYCINE, **22, 23**
- α -PHENYLGLYCOLIC ACID, **23, 48**
- Phenylhydrazine, **22, 96; 25, 38; 28, 87**
- PHENYLHYDRAZINE HYDROCHLORIDE, **22, 96**
- β -Phenylhydroxylamine, **25, 80**
- 2-PHENYLINDOLE, **22, 98**

- PHENYLLITHIUM**, **23, 83**
Phenylmagnesium bromide, **21, 79; 23, 98; 24, 84, 89; 27, 30**
 reaction with benzophenone, **23, 99**
 reaction with ethyl benzoate, **23, 98**
PHENYLMETHYLGLYCIDIC ESTER, **24, 82, 87**
1-PHENYLNAPHTHALENE, **24, 84**
PHENYLPROPARGYL ALDEHYDE, **25, 92**
PHENYLPROPARGYL ALDEHYDE ACETAL, **25, 93**
 α -**PHENYLPROPIONALDEHYDE**, **24, 87**
 2,4-dinitrophenylhydrazones of, **24, 88**
Phenyl salicylate, **26, 92**
Phenylthiosemicarbazide, **25, 38**
 α -**PHENYLTHIOUREA**, **28, 89**
N-Phenyl-*o*-toluimidyl chloride, **26, 98**
Phosgene, **27, 45**
 solution of, in toluene, **23, 13**
Phosphoric acid, **24, 30; 28, 1**
Phosphorus, red, **22, 91**
Phosphorus oxychloride, **20, 11; 22, 5; 24, 29; 25, 63; 28, 39**
Phosphorus pentachloride, **21, 86**
Phosphorus pentasulfide, **25, 36**
Phosphorus pentoxide, **25, 61, 69**
Phosphorus tribromide, **23, 32, 88**
 precautions and dangers in use of, **23, 33**
Phosphorus trichloride, **20, 106; 21, 74**
 precautions and dangers in use of, **23, 33**
Photoflood lamps, **20, 84, 104**
PTHALALDEHYDIC ACID, **23, 74**
Phthalic acid, **24, 45**
Phthalic anhydride, **20, 70; 27, 78**
PTHALIC ANHYDRIDE, TETRAIODO-, **27, 78**
PTHALIC ANHYDRIDE, TETRAPHENYL-, **23, 93**
PTHALIC MONOPERACID, **20, 70**
Phthalide, **22, 30, 62; 23, 75**
Phthalimide, potassium, **24, 46**
Phthaloyl chloride, **20, 51**
 α -**Picoline**, **20, 79; 23, 84**
PICOLINIC ACID HYDROCHLORIDE, **20, 79**
 α -**PICOLYLLITHIUM**, **23, 84**
Picric acid, **24, 65**
PINACOL, ANHYDROUS, **22, 39, 40, 41**
Pinacol hydrate, **22, 39**
Pinacolone, **22, 39, 41**
Piperidine, **23, 61; 25, 42; 27, 24; 28, 24**
Polyglyoxal, **24, 63**
Polylactic acid, **26, 4, 5**
 alcoholysis of, **26, 4**
Polymerization inhibitors, **26, 19; 28, 94**
Polyoxymethylene, **23, 30; 24, 30**
Poppyseed oil, **22, 78, 85**
Potassium, **23, 42, 45**
 precautions in use of, **24, 100**
Potassium acetate, **20, 55**
Potassium acid sulfate, **28, 31**
POTASSIUM AMIDE, **20, 91**
Potassium bromide, **20, 81, 101**
POTASSIUM *tert*-BUTOXIDE, **23, 42, 45**
Potassium carbonate, **20, 21**
Potassium chlorate, **23, 6**
Potassium cyanide, **20, 38, 44; 22, 35; 27, 41**
Potassium dichromate, **22, 45**
Potassium ethoxide, **23, 42; 26, 42**
Potassium hydrogen sulfide, **28, 16**
Potassium hypochlorite, **23, 27**
Potassium iodide, **22, 52, 71; 24, 97**
Potassium methoxide, **23, 43; 24, 6, 7, 100**
Potassium permanganate, **20, 79**
Potassium persulfate, **22, 44**
Potassium xanthate, **28, 82**
Pressure reaction, **20, 40, 81, 101; 22, 9, 19; 23, 68, 70, 71, 72, 81, 90**
 use of "booster" pump, **23, 68**
1,3-PROPANEDIONE, 1,3-DIPHENYL-, **20, 32**
1,2-PROPANEDIONE, 1-PHENYL-, **23, 1**
2-PROPANOL, 1-(2-PYRIDYL)-, **23, 83**
3-PROPANOL, 1-(2-PYRIDYL)-, **23, 85**
2-PROPANONE, 1-CHLORO-3-PHENYL-, **26, 13**
PROPIOLALDEHYDE, PHENYL-, **25, 92**
PROPIONALDEHYDE, β -ETHOXY-, DIETHYL ACETAL, **25, 1**
PROPIONIC ACID, β -3-ACENAPHTHENYL-CARBONYL-, **20, 1**
PROPIONIC ACID, β -3-ACENAPHTHOLYL-, **20, 1**
PROPIONIC ACID, β -(CHLOROFORMYL)-, METHYL ESTER, **25, 19**
PROPIONIC ACID, β , β' -METHYLIMINOBI, DIETHYL ESTER, **20, 35**
Propionic anhydride, **21, 14**
PROPIONITRILE, β -AMINO-, **27, 3**
PROPIONITRILE, β -ETHOXY-, **23, 33**
PROPIONITRILE, β , β' -IMINODI-, **27, 3**
Propionyl chloride, **24, 30**
PROTIOPHENONE, β -DIETHYLAMINO-, **23, 31**
PROTIOPHENONE, β -DIMETHYLAMINO-, **23, 30**
***n*-Propyl-*n*-butylamine**, **25, 19**
 γ -*n*-Propylbutyrolactone, **27, 68**
1-*n*-Propylpyrrolidine, **25, 19**
 δ -*n*-Propylvalerolactone, **27, 70**
Protective screen, **22, 97**
PSEUDOIONONE, **23, 78**
 bisulfite compound, **23, 79**
PSEUDOTHIODANTOIN, **27, 71**
Pseudothiodydantoin hydrochloride, **27, 72**
PYOCYANINE, **26, 86**
 by photochemical oxidation, **26, 89**
PYRAN, DIHYDRO-, **23, 25**
PYRAN, TETRAHYDRO, **23, 67, 90**

5-PYRAZOLONE, 3-AMINO-1-PHENYL-, **28**,
87
 Pyridine, **20**, **50**; **21**, **89**; **23**, **37**, **88**; **24**,
10, **92**; **27**, **38**
 anhydrous, **22**, **56**
 PYRIDINE, 2-BROMO-, **26**, **16**
 PYRIDINE, 4-ETHYL-, **27**, **38**
 1-(α -PYRIDYL)-2-PROPANOL, **23**, **83**
 1-(α -PYRIDYL)-3-PROPANOL, **23**, **85**
 PYROGALLOL 1-MONOMETHYL ETHER, **26**,
90
 oxidation with lead peroxide, **26**, **86**
 various methods for preparation, **26**,
91
 Pyrolysis, **25**, **38**
 PYROTARTARIC ACID, **26**, **54**
 PYRROLE, 2,4-DIMETHYL-3-ACETYL-5-
 CARBETHOXY-, **21**, **68**
 PYRROLE, 2,4-DIMETHYL-3-ETHYL-, **21**, **67**
 PYRROLE, 2,4-DIPHENYL-, **27**, **33**
 PYRROLIDINE, 1-BUTYL-, **25**, **14**
 2-PYRROLIDONE, 1,5-DIMETHYL-, **27**, **28**
 Pyruvic acid, **24**, **72**

 QUINACETOPHENONE, **28**, **42**
 QUINOL, DIACETATE, **28**, **68**
 Quinoline, **21**, **87**
 QUINOLINE-4-CARBOXYLIC ACID, 2-HY-
 DROXY-, **28**, **70**
 QUINOLINE, 4,7-DICHLORO-, **28**, **38**
 QUINOLINE, 2,4-DIMETHYL-, **28**, **49**
 QUINOLINE, 6-METHOXY-8-NITRO, **27**, **48**
 Quinones, **22**, **37**

 Raney nickel-aluminum alloy, **27**, **68**
 RANEY NICKEL CATALYST, **21**, **15**; **22**, **9**,
12; **23**, **68**, **71**, **81**, **90**; **25**, **10**; **27**, **13**,
18, **22**, **28**, **33**
 Rearrangement, Claisen, **25**, **49**
 ω,ω -dichloroacetophenone to mandelic
 acid, **23**, **49**
 retropinacol, **22**, **41**
 Red lead, **21**, **1**, **3**
 Reduction, by amalgamated zinc and
 hydrochloric acid, benzoin to stil-
 bene, **23**, **86**
 by ferrous sulfate, **28**, **11**
 by hydrogen and Raney nickel, at
 high pressures, **22**, **9**
 at low pressures, **22**, **12**
 alkoxynitrobenzenes to alkoxyani-
 lines, **25**, **10**
 benzyl cyanide to phenethylamine,
 23, **71**
 dihydropyran to tetrahydropy-
 rane, **23**, **90**
 pseudoionone to hexahydropseudo-
 ionol, **23**, **81**
 with simultaneous amination by
 ammonia, acetophenone to α -
 phenylethylamine, **23**, **68**

Reduction—*Continued*
 by hydrogen sulfide, **23**, **7**
 by sodium sulfide and ammonium
 chloride, **25**, **5**
 by stannous chloride, Stephen reduc-
 tion of β -naphthonitrile to β -naph-
 thaldehyde, **23**, **63**
 by zinc and alkali, **22**, **28**
 by zinc and ammonium chloride, **25**,
 80
 by zinc and hydrochloric acid, **20**, **57**
 Clemmensen, **20**, **57**
 electrolytic, **21**, **10**
 of a double bond by sodium amalgam,
 22, **90**
 of a hydroxylamino acid to an amino
 acid by hydroxylamine, **22**, **26**
 of an imide chloride to an aldehyde,
 26, **98**
 of a nitro compound by stannous
 chloride, **22**, **32**; **25**, **66**
 of a nitro compound to an amine, **22**,
 9; **25**, **5**, **55**; **28**, **11**, **14**
 of a nitro compound to an azo com-
 pound, **22**, **28**
 of a nitro compound to a hydroxyl-
 amine, **25**, **80**
 of nitroguanidine with zinc, **26**, **7**
 over palladium, **26**, **32**, **46**
 Rosenmund (Pd-BaSO₄), **21**, **84**, **110**
 Reductive alkylation, of cyanoacetic
 ester with butyraldehyde, **26**, **32**
 of ethanalamine with acetone, **26**, **38**
 Reformatsky reaction, **21**, **51**
 Reimer-Tiemann reaction, **22**, **63**
 Replacement, aldehyde group by hy-
 droxyl, **26**, **90**
 amino group by a bromine atom
 (diazo reaction), **24**, **22**
 amino group by hydroxyl group (diazo
 reaction), **23**, **11**; **25**, **55**
 bromine atom by an amino group,
 28, **46**
 bromine atom by a cyano group, **21**,
 89; **23**, **33**; **28**, **34**
 bromine atom by a hydroxyl group,
 23, **76**
 carboxyl group by bromine, **26**, **53**
 chlorine atom by an amino group, **22**,
 6
 chlorine atom by a cyano group, **24**,
 97; **25**, **66**
 chlorine atom by a sulfone group, **22**,
 31
 chlorine atom by a thiol group, **28**, **14**
 diazonium group by a nitro group, **28**,
 52
 diazonium group by a thiol group, **27**,
 81
 glycosidic bromine atom by a hy-
 droxyl group, **25**, **53**

Replacement—*Continued*

- glycosidic hydroxyl group by a bromine atom, **22**, 2
- hydrogen atom by a cyano group, **22**, 35
- hydroxyl group by an amino group, **22**, 19
- hydroxyl group by a bromine atom, with phosphorus tribromide, **23**, 32
 - with phosphorus tribromide and pyridine, **23**, 88
- hydroxyl group by a chlorine atom, **22**, 5; **24**, 28; **28**, 39, 65
 - with phosphorus oxychloride, **28**, 39
 - with thionyl chloride, **25**, 84
- hydroxyl group by chlorine or bromine with acetyl halides, **23**, 100, 102
- nitro group by a methoxyl group, **22**, 35
- sulfonamide group by hydrogen, **24**, 48, 49
- RESACETOPHENONE, **21**, 103
- Resorcinol, **21**, 23, 103; **27**, 21
- α -RESORCYLIC ACID, **21**, 27
- RHODANINE, **27**, 73
- Ring opening by hydrolysis with barium hydroxide, **22**, 91
- Rosenmund synthesis, aldehyde, **21**, 84, 110
 - nitrile, **21**, 89
- Salicylaldehyde, **28**, 24
 - purification of, **28**, 25
- Salicylanilides, from various amines, **26**, 93
- o*-SALICYLOTOLUIDE, **26**, 92
- SALICYL-*o*-TOLUIDE, **26**, 92
- Salol, **26**, 92
- Salt bath for heating, composition of, **21**, 90
- Sand as diluent to prevent caking, **22**, 98; **25**, 63
- Sandmeyer reaction, **24**, 22
- Saponification, of an ester, **26**, 30
 - with sodium cyanide, **26**, 54
 - of ethyl linoleate, **22**, 78
 - of ethyl linolenate, **22**, 84
 - of natural oils, **22**, 75, 79, 82
 - of *p*-nitrobenzyl acetate, **24**, 81
- Screen, protective, **22**, 97
- Seal, rubber tube, for stirrer shaft, **21**, 40
- SEBACAMIC ACID, METHYL ESTER, **25**, 71
- Sebacamide, **25**, 95
- Sebacic acid, **25**, 95
- SEBACONITRILE, **25**, 95; **27**, 18
- Selenious acid, **24**, 61, 62
- Selenium, **24**, 63; **27**, 33
 - powdered, black, **24**, 90
- Selenium compounds, ease of oxidation, **24**, 91
 - precautions when working with, **24**, 89
 - sensitivity to light, **24**, 90
- Selenium dioxide, **24**, 62
- Selenocresols, **24**, 91
- Selenophenol, **24**, 89
- Selenophenols from hydrolysis of aryl selenocyanate, **24**, 91
- SENECIOIC ACID, **23**, 27
- Separatory funnel, large, construction of, **23**, 105
- DL*-SERINE, **20**, 81
- Shaking extractor, **23**, 78
- Silver acetate, **20**, 15
- Silver carbonate, **25**, 54
- Silver salt, drying of a, **26**, 53
 - of methyl hydrogen adipate, **26**, 52
- Skellysolve B, **24**, 70
- Skraup reaction, **27**, 48
- Snyder column, **20**, 68
- Sodamide, *see* SODIUM AMIDE
- Sodium, **20**, 7, 74, 88; **21**, 42, 60, 68, 99; **22**, 92; **23**, 16, 18, 20, 53, 95, 97; **24**, 60, 87; **25**, 11; **28**, 9, 44, 50, 87
- Sodium acetate, **20**, 6, 11, 56, 75; **22**, 54; **24**, 79; **27**, 10, 36; **28**, 73
- Sodium amalgam, **22**, 90, 92
- SODIUM AMIDE, **20**, 40, 87; **22**, 94; **23**, 20; **24**, 83; **25**, 25; **28**, 8, 44
 - grinding, **20**, 41, 88; **22**, 95
 - handling, **20**, 41, 88
 - residues, destruction of, **20**, 90
- Sodium anilide, **28**, 50
- Sodium arsenite, **26**, 61
- Sodium azide, **24**, 94
- Sodium bicarbonate, **20**, 26; **23**, 78
- Sodium bisulfite, **20**, 43; **23**, 78, 79; **24**, 2, 62; **27**, 20; **28**, 85
- Sodium bromide, **24**, 23
- Sodium carbonate in preparation of an acid chloride, **25**, 87
- Sodium chloroacetate, **27**, 74
- Sodium cyanide, **20**, 44; **22**, 13, 23; **23**, 33; **24**, 9; **25**, 66; **27**, 21
- Sodium cyclohexoxide, **25**, 30
- Sodium dichromate, **24**, 1; **28**, 63
- Sodium ethoxide, **20**, 7, 9, 33; **22**, 26; **23**, 35, 79; **24**, 87; **25**, 44; **26**, 29; **28**, 87
 - by "inverse" procedure, **23**, 18
- Sodium hypochlorite, **22**, 73
- Sodium isopropoxide, **25**, 29
- SODIUM *L*-MENTHOXIDE, **23**, 52
- Sodium methoxide, **20**, 14, 74
 - by "inverse" procedure, **23**, 18
- Sodium nitrite, **21**, 31, 67; **22**, 96; **23**, 11; **24**, 22, 27, 56; **27**, 81; *see also* Diazotization
- Sodium *p*-nitroperbenzoate, **23**, 66
- Sodium peroxide, **23**, 65
- Sodium powder, **20**, 8; **23**, 96; **25**, 86

- Sodium 2-pyridinediazotat, **26, 18**
 Sodium sulfate, anhydrous, **22, 57; 28, 12**
 Sodium sulfide, **25, 5; 28, 14**
 Sodium sulfite, **23, 78; 24, 23, 33**
 Sodium thiocyanate, **22, 17**
 Sodium zincate, **22, 28**
 SORBIC ACID, **24, 92**
 Spray trap, **23, 1**
 Stannic chloride, **25, 33**
 Stannous chloride, anhydrous, **23, 64**
 Stannous chloride dihydrate, **22, 32; 23, 63; 25, 55**
 Starch-iodide test paper, use in following diazotizations, **24, 23**
 Steam distillation, **20, 2; 28, 11**
 STEAROLIC ACID, **27, 76**
 Stephen reduction, **23, 63**
trans-STILBENE, **22, 50; 23, 86**
 STILBENE DIBROMIDE, **22, 50**
 Stirrer, air, **25, 96**
 brass, **21, 44**
 glycerol-sealed, **21, 40**
 Hershberg, **20, 8; 22, 23, 74; 23, 33**
 "Lightnin" mixers, **21, 97**
 Monel-metal, **20, 99**
 stainless-steel, **23, 54**
 Tru-bore, **25, 67**
 Strecker synthesis, **22, 13, 23; 24, 9**
 STYRENE, *m*-CHLORO-, **28, 31**
 Styrenes, **28, 31, 33**
 Sublimation in vacuum desiccator, **25, 57**
 Succinic anhydride, **20, 1**
 Sulfanilamide, **24, 47, 48, 49, 50**
 SULFIDE, *bis*-(*p*-NITROPHENYL-), **28, 82**
 Sulfonation of *o*-toluidine, **27, 88**
 SULFONE, **22, 31**
 Sulfur dioxide, **22, 92**
 Sulfuric acid, **22, 48, 49; 23, 11**
 as cyclizing agent, **25, 14, 73**
 fuming, **21, 27**
 Sulfuryl chloride, **22, 17**
 Sunflower seed oil, **22, 75, 80**
 Superheater for steam, **23, 64**
- d*-Tartaric acid, **22, 65; 23, 79, 80**
 TARTARIC ACID DINITRATE, **22, 65**
 TEREPTHALALDEHYDE, **20, 92**
 TEREPTHALIC ACID, **26, 95**
 esterification of, **26, 96**
 various methods of preparation, **26, 96**
 2,3,4,6-TETRAACETYL- α -*d*-GLUCOPYRANOSYL BROMIDE, **22, 1; 25, 53**
 1,2,3,4-TETRAACETYL- β -*d*-GLUCOSE, **22, 56**
 2,3,4,6-TETRAACETYL- β -*d*-GLUCOSE, **25, 53**
 Tetraacetylglucose-6-mononitrate, **22, 58**
 TETRABROMOSTEARIC ACID, **22, 76**
- $\alpha,\alpha,\alpha',\alpha'$ -TETRABROMO-*p*-XYLENE, **20, 92**
 Tetrachloroethane, **23, 57**
 precautions in use of, **23, 58; 25, 69**
n-TETRADECYL *p*-BROMOBENZENESULFONATE, **20, 51**
n-TETRADECYL *p*-TOLUENESULFONATE, **20, 51**
 Tetrahydrofurfuryl alcohol, **23, 25, 88; 25, 84; 26, 83**
 TETRAHYDROFURFURYL BROMIDE, **23, 88**
 TETRAHYDROFURFURYL CHLORIDE, **25, 84**
 β -(TETRAHYDROFURYL)-PROPIONIC ACID, **27, 68**
 TETRAHYDROPYRANE, **23, 67, 90**
 Tetrahydroquinoline, **26, 40**
 TETRAIDODOPHTHALIC ANHYDRIDE, **27, 78**
 Tetralin, **20, 94**
 α -TETRALONE, **20, 94; 24, 85**
 Tetramethylenediamine, methylation of, **25, 91**
 2,3,4,6-TETRAMETHYL-*d*-GLUCOSE, **20, 97**
 TETRAMETHYLMETHYLGLUCOSIDE, MIXTURE OF α AND β , **20, 100**
 Tetramethyl- α -methylglucoside, **20, 99**
 TETRANITROMETHANE, **21, 105**
 Tetranitromethane as reagent for detecting double bonds, **21, 107**
 TETRAPHENYLCYCLOPENTADIENONE, **23, 92, 93**
 TETRAPHENYLDIHYDROPHthalic ANHYDRIDE, **23, 93**
 TETRAPHENYLPHthalic ANHYDRIDE, **23, 93**
 β -(α -Thenoyl)-propionic acid, **27, 70**
 THIAZOLE, 2,4-DIMETHYL, **25, 35**
 4-THIAZOLIDONE, 2-IMINO-, **27, 71**
 Thioacetamide, **25, 36**
 Thiocarbamic acid, **26, 35**
m-THIOCRESOL, **27, 81**
 Thionyl chloride, **20, 77; 21, 78; 23, 55; 24, 21; 25, 19, 58, 71, 84, 87; 26, 57**
 Thiophene, **28, 1**
 Thiophenols, **24, 91**
 Thiourea, **21, 36; 22, 59; 27, 71**
dl-THREONINE, **20, 101**
 Tin, **20, 19**
 TOLAN, **22, 50**
o-Tolidine, **21, 32, 34**
o-TOLUALDEHYDE, **26, 97**
 various methods of preparation, **26, 99**
o-Toluanilide, **26, 97**
 Toluene, **20, 66; 22, 53; 23, 12, 52, 65**
 TOLUENE, α -CHLORO-2-HYDROXY-5-NITRO-, **20, 59**
p-Toluenesulfonic acid, **24, 72; 26, 19; 28, 73**
m-TOLUENESULFONIC ACID, 6-AMINO-, **27, 88**
p-Toluenesulfonyl chloride, **20, 50**
m-TOLUENETHIOL, **27, 81**

- o*-TOLUIC ACID, **27, 84**
p-TOLUIC ACID, **27, 86**
 α -TOLUIC ACID, α -AMINO, *dl*, **22, 23**
 α -TOLUIC ACID, *o*-CARBOXY, **22, 61**
 α -TOLUIC ACID, 2,4,6-TRIMETHYL-, **25, 65**
m-Toluidine, **21, 108; 27, 81**
o-Toluidine, **23, 43; 26, 92; 27, 88**
p-Toluidine, **22, 16**
m-TOLUIDINE, *N*-BENZYL, **21, 108**
p-Toluidine sulfate, **22, 17**
o-TOLUIDINESULFONIC ACID, **27, 88**
m-TOLYLBENZYLAMINE, **21, 108**
o-Tolylbenzylamine, **21, 109**
p-Tolylbenzylamine, **21, 109**
m-Tolyl ethyl xanthate, **27, 82**
o-Tolylmagnesium bromide, **26, 98**
m-TOLYL MERCAPTAN, **27, 81**
p-TOLYLTHIOUREA, **22, 17**
 Toxicity, **20, 97; 23, 58; 24, 89**
 Transesterification, **26, 19**
 polylactic acid and allyl alcohol, **26, 4**
 Trap for absorbing gases, **23, 13, 55, 102**
 1,3,5-TRIACTYLBENZENE, **27, 91**
 1,2,4-TRIAZOLE, 3-AMINO-, **26, 11**
 1,3,4-TRIAZOLE, 1-AMINO-, **24, 12**
 TRIBIPHENYL CARBINOL, **23, 95, 97**
sym.-Tribromoaniline, **24, 51, 52**
 3,4,5-Tribromobenzoyl chloride, **23, 66**
 3,4,5-TRIBROMOBENZOYL PEROXIDE, **23, 66**
N-TRICARBOXYLIC ESTER, **24, 58, 60**
 1,2,4-Trichlorobenzene, **26, 92**
 2,4,6-TRIETHYLBENZALDEHYDE, **23, 60**
 1,3,5-Triethylbenzene, **23, 60**
 2,4,6-Triethylphenylacetone, **25, 67**
m-Trifluoromethylphenylcarbinol, **23, 30**
 2,4,6-TRIISOPROPYLBENZALDEHYDE, **23, 60**
 1,3,5-Triisopropylbenzene, **23, 60**
 Trimerization, **27, 93**
 2,4,6-TRIMETHYLBENZALDEHYDE, **21, 110; 23, 57, 59**
 TRIMETHYLENE BROMIDE, **20, 25; 23, 16; 24, 46**
 Trimethylene chlorobromide, **26, 40**
 Trimethylthiourea, **21, 84**
 2,4,7-TRINITROFLUORENONE, **28, 91**
 TRIPHENYLBROMOMETHANE, **22, 57; 23, 102**
 TRIPHENYL CARBINOL, **23, 98, 100**
 TRIPHENYLCHLOROMETHANE, **22, 56; 23, 100, 102**
 TRIPHENYLMETHYL BROMIDE, **22, 57; 23, 102**
 TRIPHENYLMETHYL CHLORIDE, **22, 56; 23, 100, 102**
 Tritylation of glucose, **22, 56**
 TRITYL BROMIDE, **22, 57; 23, 102**
 TRITYL CHLORIDE, **22, 56; 23, 100, 102**
 6-TRITYL β *D*-GLUCOSE-1,2,3,4-TETRA-ACETATE, **22, 56**
- Two-bulb distilling flask, **20, 20**
 Ullmann reaction, **26, 51**
 Ullmann synthesis, **20, 45**
 UNDECYL ISOCYANATE, **24, 94**
n-Undecyl mercaptan, **21, 38**
o-Undecylphenol, **20, 58**
p-Undecylphenol, **20, 58**
 Urea, **23, 11, 25**
 UREA, 1-METHYL-1-(1-NAPHTHYL)-2-THIO-, **27, 58**
 UREA, 1-PHENYL-2-THIO-, **28, 89**
 Urethan, **24, 60**
 Uric acid, **23, 6**
- Vacuum desiccator, "dumb-bell" type, **23, 105**
 VALERALDEHYDE, δ -HYDROXY-, **27, 43**
 VALERIC ACID, δ -BROMO-, METHYL ESTER, **26, 52**
 Valerylchlororesorcinol, **20, 58**
o-Valerylphenol, **20, 58**
p-Valerylphenol, **20, 58**
dl-VALINE, **20, 106**
 Vanillin, **22, 90**
 γ -Veratrylbutyric acid, **26, 29, 30**
 Vigreux column, **20, 22, 52**
 Vinyl acetate, **23, 9**
 VINYLACETIC ACID, **24, 96**
 VINYL CHLOROACETATE, **28, 94**
- Walnut oil, **22, 85**
 Water separator, **23, 38; 25, 46; 26, 4**
 Wax, bayberry, **20, 67**
 myrtle, **20, 68**
 Widmer column, **20, 7, 9, 22, 41, 52, 68, 84**
 Wilson rings, **20, 52**
 Wire helices, **20, 96**
 Wurtz-Fittig reaction, **25, 11**
- Xylene, **23, 96**
 dry, **20, 8, 9**
 purified for Rosenmund reduction, **21, 85**
o-Xylene, **27, 84; 28, 22**
p-Xylene, **20, 92**
o-XYLENE, 4-BROMO-, **28, 22, 46**
 3,4-XYLIDINE, **28, 46**
- Yeast, **22, 53**
- Zinc, **20, 57; 22, 77, 83**
 amalgamated, **20, 57; 23, 86**
 Zinc chloride, **20, 52; 22, 19**
 anhydrous, **21, 103; 22, 98; 24, 18; 28, 60**
 Zinc cyanide, **23, 57**
 Zinc dust, **21, 51, 68; 22, 28; 23, 86; 25, 80**
 activation of, **26, 7**
 purification of, **21, 52**

NOMENCLATURE

Preparations are listed under the names which are used commonly for the compounds. For the convenience of those who wish to make a complete survey of the literature on any preparation, the *Chemical Abstracts* **indexing name** for each compound is given as a subtitle when that name differs from the title of the preparation.

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TABLE OF CONTENTS

	PAGE
2-ACETOTHIENONE	1
2-ACETYLFUORENE	3
9 ACETYLPHENANTHRENE	6
2-ALLYLCYCLOHEXANONE	8
<i>o</i> -AMINO BENZALDEHYDE	11
<i>p</i> AMINOPHENYL DISULFIDE	14
BENZOYL DISULFIDE	16
9-BROMOPHENANTHRENE	19
4 BROMO- <i>o</i> -XYLENE	22
3-CARBETHOXYCOUMARIN	24
<i>p</i> -CHLOROACETYLACETANILIDE	26
<i>m</i> CHLOROPHENYLMETHYLCARBINOL	28
<i>m</i> CHLOROSTYRENE	31
9 CYANOPHENANTHRENE	34
<i>trans</i> 1,2 CYCLOHEXANEDIOL	35
4,7 DICHLOROQUINOLINE	38
2,5 DIHYDROXYACETOPHENONE	42
DIISOVALERYLMETHANE	44
3,4-DIMETHYLANILINE	46
2,4 DIMETHYLQUINOLINE	49
1,4-DINITRONAPHTHALENE	52
DIPHENYLACETONITRILE	55
ETHYL AZODICARBOXYLATE	58
ETHYL ETHOXYMETHYLENEMALONATE	60
FLUORENONE-2-CARBOXYLIC ACID	63
HEXAMETHYLENE CHLOROHYDRIN	65
HYDROQUINONE DIACETATE	68
2 HYDROXYCINCHONINIC ACID	70
<i>dl</i> ISOPROPYLIDENEGLYCEROL	73
METHYL 4 KETO-7 METHYLOCTANOATE	75
4 NITRO-1-NAPHTHYLAMINE	80
<i>p</i> NITROPHENYL SULFIDE	82
PHENANTHRENE 9 ALDEHYDE	83
1 PHENYL-3-AMINO 5 PYRAZOLONE	87
α PHENYLTHIOUREA	89
2,4,7 TRINITROFLUORENONE	91
VINYL CHLOROACETATE	94
SUBJECT INDEX FOR VOLUMES 20-28	99

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